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CONTRACT NAS 7-436 • INTERIM REPORT 06641-6014-R000 • NOVEMBER 1967

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ADVANCED VALVE TECHNOLOGY

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VOLUME II MATERIALS COMPATIBILITY AND LIQUID PROPELLANT STUDY

PREPARED FOR
CHIEF, LIQUID-PROPULSION TECHNOLOGY, CODE RPL
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C.

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TRW SYSTEMS
ONE SPACE PARK • REDONDO BEACH • CALIFORNIA

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FOREWARD

This report was prepared by TRW Systems Group, Redondo Beach, California, and contains the results of work accomplished between January 1967 to November 1967. The report is published in two volumes. This volume reports the results of the work accomplished on the Liquid Propellant Study. The work was performed for the Chief, Liquid Propulsion Technology, Code RPL; Headquarters, National Aeronautics and Space Administration. The Headquarters Project Manager is Mr. Frank E. Compitello. The program was administered under the technical direction of Mr. Louis R. Toth of the Jet Propulsion Laboratory, Pasadena, California.

The work performed on the program was accomplished by TRW Systems Group, Power Systems Division, Technology Laboratory. Mr. R. J. Salvinski of the Auxiliaries and Component Technology Department is the Program Manager. Technical efforts provided for the work reported in Volume II of this program by the several TRW Systems Group personnel are acknowledged.

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ABSTRACT

This report describes the work performed by TRW Systems Group during a 12-month period with the objective of advancing the state of the art of valves used on spacecraft liquid propulsion systems. Current problems and future requirements relating to valve design, operation and test were determined. Interviews were held with personnel of NASA, Air Force, and prime manufacturers of propulsion systems to identify valve problems. New technology was utilized where necessary, to solve problems. Areas of study included propellant valves, valve actuators, and fluidic controls, instrumentation and measurements, liquid propellants and thin polymeric films. The results of the effort are reported in two volumes.

Volume I - Spacecraft Valve Technology

The valve technology study included problem analysis and problem identification; a review of reliability techniques in the specific area of valve redundant systems; seal leakage; and conceptual studies. A bipropellant valve concept requiring no-moving parts is described. Surface tension of liquids to provide valve sealing was studied and test data presented. A no-moving parts valve based on the principle of electroplating to effect a zero leak shutoff and throttling function was fabricated and tested. Conceptual tests were performed in a simple shutoff valve utilizing the interaction of magnetic fields on liquids to shift the liquid from off or on flow positions.

The applications and limitations of valve actuators were determined and new technology reported included a high speed actuator study. Reported are a monopropellant and bipropellant actuator, and a thermal actuator concept. The monopropellant actuator was fabricated and tested to determine feasibility. An investigation of thin film beryllium for use as an electrical conductor at low temperatures showed constant electrical resistance within 1 percent over a temperature range from ambient to liquid N_2. Actuation techniques studied include electromechanical, hydraulic, pneumatic, chemical and thermal.

The advantages of applying fluidics to liquid propulsion systems are reduced size, and weight, with increased reliability. The most common fluidic devices were studied relative to configuration, performance, fabrication and materials, specific functional parameters, propellant compatibility, and the space environment. The technical problems and standard application criteria were reviewed, and the analytical techniques used to synthesize and design fluidic systems from the components level were outlined. Conceptual studies were initiated in the areas of pressure references and fluid flow regulation. An extensive bibliography is included.

In-flight leakage and valve positioning measurements criteria were established. The application of thin polymeric films as compatible coatings and valve seals were considered. In support of the work, an investigation was made of the formation kinetics of the films applied by electron bombardment techniques.

Volume II - Materials Compatibility and Liquid Propellant Study

This volume includes the results of surveys pertaining to the materials compatibility, shock sensitivity, lubricity, viscosity, radiation tolerances, and effects of leakage for 21 liquid propellants in present use or anticipated use within the next ten years. The information contained herein results from review of the literature listed in the Bibliography at the conclusion of this section. A new test method was studied pertaining to the evaluation of materials compatibility with propellants for long term storage.

Also included in this volume is a report on clogging of filters and orifices during flow with N_2O_4.

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MATERIALS COMPATIBILITY AND LIQUID PROPELLANT STUDY

I. MATERIALS COMPATIBILITY

INTRODUCTION

The information contained in this section has been extracted from the best technical sources available; these sources are referenced in the bibliography at the end of the compatibility section. Materials compatibility data derived from these sources are generally the result of laboratory scale bottle tests involving immersion of materials in propellants under static conditions. For the most part, these data are fairly consistent, but many instances exist where data are contradictory or differing in degree of compatibility. Also, in most cases the data report only the effects of propellant exposure, and do not reflect the functionality of the material after exposure.

Where differences were noted, acceptance of information was based on multiple sources, appropriate procedures, availability of service data, and recentness of evaluation. Unless specifically noted, data not meeting these criteria have not been included.

Propellant compatibility data contained in the following reference is included:

> "Advanced Valve Technology," Interim Report, September 1, 1965 to November 1, 1966, TRW Systems Report No. 06641-6004-R000.

The work presented in this report represents a continuation of the referenced study, however, where possible the data was updated to include more recent information.

DISCUSSION

In the course of the literature search performed, several areas requiring early additional effort became apparent. Basically, it was noted that the testing performed to obtain the desired data shared a common failing: there was no conformity of method, no procedural approach to the problem of the compatibility test, and little assessment of the effects of impurities in the propellants. For example, some long term compatibility data were generated based on actual immersion for one year periods, while others were conducted for shorter periods of time, and data extrapolated to one year. Short term compatibility, in some cases, denotes ability to survive propellant exposure for two to four weeks. In other cases, it is defined as the ability to withstand propellant splash or fumes for designated periods of time. In very few cases, has the effect of the material on the propellants been determined, and the initial processing of the test specimen is seldom recorded. The variations do not reflect on the multitude of investigators, but rather on the void which exists with respect to test standards to which work has been performed.

The compatibility of materials to the liquid propellants primarily takes on three aspects:

- Slow to rapid chemical or electrochemical reaction between metals and the propellants leading to corrosion and loss of strength of the metals and/or degradation of the propellants.
- Slow to rapid chemical reaction between non-metals and the propellants leading to degradation and loss of strength.
- Rapid chemical reaction between all types of materials and the propellants leading to explosion or fire within the system.

Each of these undesirable aspects of materials compatibility have been investigated by various organizations, and the data reported. However, there are quite often differing and sometimes conflicting points of view concerning the compatibility and use of a specific material. This conflict of opinion frequently arises not from incorrect data or interpretation, but rather from a lack of a common reference point. In particular,

Failure to delineate all of the testing parameters and procedures, and of not characterizing the test fluid sufficiently, can lead to widely different results, each of which, however, are valid within the context of the experiment performed. Two illustrations are presented as cases in point:

1. Corrosion

Most of the data on corrosion of metals are given in terms of depth of material removed per unit time. Usually the data are presented as penetration in mils per year (MPY). Not so frequently, however, is a description given of the type of corrosion, or of the localized severity. Inasmuch as a MPY removal figure implies a general, overall corrosion of the metal, failure of the investigator to remark that the greatest amount of corrosion occurred as pitting or intergranular attack could lead a designer, using the compatibility data, to arrive at an erroneous conclusion regarding the service life of the metal with respect to the propellant in question. It is suggested that a common corrosion description, such as that proposed by Champion*, should be employed when reporting data of this nature.

2. Propellant and Test Specimen Characterization

It is well known that relatively minor impurities can cause gross changes in the characteristics of liquid propellants. Failure to properly analyze and report the chemical makeup of the test fluid utilized in the experiments can lead to unwarranted conclusions. As an example, several metals are compatible with OF_2. If, however, the OF_2 is contaminated with water, hydrogen fluoride is formed which is particularly reactive toward metals which cannot form adherent, passive protective films against the fluoride ion. Thus, failure to analyze the HF content of the OF_2 can lead to erroneous conclusions regarding its compatibility.

* General Reference, No. 1, Page 1-105.

This same type of problem has occurred in the testing of the impact sensitivity of LOX with various metals. Lack of close control in insuring contamination free metal samples and the testing apparatus has led to some conflict of data in this area.

Since contamination can occur during transport and handling of samples and test equipment, it is suggested that the test fluids be analyzed as used, and any possible contamination path be noted.

From the standpoint of the valve designer involved in the process of material selection as one portion of the component design, the available data do not provide the necessary information from which to make rapid and automatic selections. In order for such information to be intelligently used, it must be supplemented in areas which are currently lacking.

For example, the data presently available do not normally distinguish between static and dynamic compatibility, either in respect to the test methods employed, or where a material's use is approved, in respect to that material's potential application. In many instances it may be assumed that the mechanism for potential failure of a particular material is augmented by the mechanical action of adjoining component materials and/or the erosive effects of the flowing propellant itself. Specifically, a material appropriate for use as a static parking within a given valve assembly may be completely incompatible, in the identical propellant service, when used as a sliding seal or an impact seal. For example, butyl rubber seals and O-rings have proven to be excellent static seals for containment of nitrogen tetroxide, even though the material itself is completely incompatible with the propellant. The sealing ability of the material is enhanced by the fact that it swells and becomes gummy in contact with N_2O_4. On the other hand, once the material has been exposed to N_2O_4, it could never survive a sliding motion. Data regarding these conditional aspects of compatibility are not presently documented. Similarly, the effects of temperature, pressure and propellant phase variations have seldom been treated in establishing compatibility.

A second distinct information void, with respect to material compatibility, exists in the area of historical data accumulation. The primary source of the data presented is the laboratory test. This is seldom supplemented by field information which should be extensive.

A search of the actual materials employed in varying configurations, environments, and propellant service would greatly aid in establishing a realistic confidence level for new valve designs. A detailed search, though beyond the scope of the present program, would not only serve as an early source of dynamic use-data, but would provide confirmation of, and give direction to, successive laboratory test effort. An attempt was, therefore, made in the course of the Advanced Valve Technology Program, to survey briefly the available experience through direct interview of cognizant personnel.

The data presently contained in this survey report attempt to correct some of these shortcomings by including what supplementary information could be readily obtained. It is felt that a more extensive program will permit sounder initial component designs with a minimum expenditure of development time and cost and is, therefore, warranted.

MATERIALS COMPATIBILITY TEST METHODS

There is a serious lack of precise compatibility data for both short term and long term storage of the more energetic propellants in the accepted materials of construction. The shortcomings of present compatibility data and the lack of standard, unified test methods, reporting and compilation has been discussed in the introduction. The more serious problem is that of obtaining reliable data for long term requirements necessary for upcoming spacecraft missions, which have operating lifetimes of up to ten years. It is generally accepted that short term, accelerated storage and testing do not give data which can be reliably extrapolated to longer mission lives. Compatibility testing in real time is prohibitively expensive, and may be outmoded by state of the art advances from the initiation of testing, which may render the evaluation obsolete.

Under this program a laser technique was studied which may prove to circumvent the traditional shortcomings of conventional compatibility testing. This technique is holographic interferometry. This test method records the fringe pattern of the propellant adjacent to the sample. The distortion of the fringe pattern with time represents corrosion mapping. The theory of holographic processes have been extensively discussed in the literature* and will not be detailed.

However, it is significant to note that a hologram is able to record a complex optical wave so that when the hologram is reilluminated later, another optical wave is created identical to the original in both phase and amplitude. It is this property which makes it possible to use a hologram to generate either the test beam, or a comparison beam, or both as an interferometric analytical technique.

Holographic interferometry may be considered as a form of common path interferometry (normally not used with conventional light sources due to cell size, configurations, optical inhomogeneities, etc.), except that the

*E.N. Leith and J. Upatnieks, J. Opt. Soc. Amer., 52, 1123 (1962); 53, 377 (1963); 54, 1295 (1964).

test and comparison beams are separated in time. It is the use of this feature, either double exposure or "stored beam" interferometry, that is of interest in their application to compatibility and corrosion investigation.

Thus far, the techniques have been utilized in applications to electro-mechanical processes*. In the case of double exposure interferometry, the holographic record represents only one instant of time, and it is not possible to view changes as they occur in the subject without making new holograms. However, if only the comparison beam is holographically recorded and "stored", and the reconstructed comparison beam is compared with the actual subject and test beam, then the real time behavior of the subject can be seen interferometically. Thus, "stored beam' holographic interferometry offers not only real time information, but provides a means for acquiring time-lapse or moving picture records during the course of the reaction.

There are several advantages of the "stored beam" holographic interferometric method over the classical methods: alignment and preparatory procedures are far less critical, the common path nature provides significant flexibility and irregular shaped and imperfect optic elements and cells may be used. Furthermore, by the use of diffusers, three-dimensional information may be obtained. Thus, investigation of localization of corrosion and non-rotational symmetrical activities can be observed, as well as the use of assymetric samples.

These advantages then, enable one to observe changes which occur in a subject as a function of time, and since the aspects of the subject do not change the interference pattern as a function of time, a technique is

* L. O. Heflinger, R. F. Wuerker and R. E. Brooks, Appl. Phys., 37, 642 (1966).

R. W. Brooks, L. O. Heflinger and R. F. Wuerker, Appl. Phys., Letters, 7, 248, (1965).

available which is able to measure subtle changes in very complex samples incapable of being explored with any of the classical methods of interferometry.

While it is true that this method has thus far been utilized only for electromechanical changes with an external driving force, there is no reason that subtle interactions between materials and their potentially corrosive environment cannot be observed also. Thus, elucidation of the onset and nature of corrosion should be observable. The rating of the suitability of a material can be evaluated with far more precision than with any other available method.

RECOMMENDATIONS

In order to provide greater utility for the valve component designer, it is recommended that a study be authorized and implemented which will achieve the following results:

1. Establishment of realistic criteria for valve component materials and definition of parameters which can affect performance under those conditons.

2. Establishment of test methodology (see section on test methods), the test fluid and test specimen, and which will provide more meaningful information to the designer relative to the performance of materials under specified conditions.

3. Establishment of a procedure for documenting and reporting compatibility data such that extraneous data will be minimized, and pertinent data will be presented in their most useable form.

The proposed program would not only take advantage of all existing data, but would identify the effects of material processing variables as well as propellant impurities. It would also introduce advanced concepts of testing to more accurately determine the functionality of materials during and after propellant exposure, and under static and dynamic conditions.

The recommended program will also consider the long duration mission such as the ten year space flight to the outer planets. Past applications have usually involved storage and operation times on the order of days, weeks or months. This has generally enabled design personnel to instigate full duration tests of new materials during the design phase. Full duration tests of materials for a ten year space flight might well become obsolete during the test phase due to rapid technological advances in material developments. Consequently, the proposed program will attempt to generate accelerated test methods that will provide valid data applicable to long term materials and component compatibility with propellants.

It is felt that the outlined program will provide a significant advance in an area of vitally needed data where the approach taken to date has been seriously inadequate.

PROPELLANT RATING CHART (TABLE 1-1)

In this chart the severity of the problems associated with each propellant were assessed and values assigned to the various combinations of propellants and parameters according to the following definitions:

RATING	DEFINITION
1	A value of 1 was assigned to those combinations with which a serious problem exists; i.e., one for which there is no satisfactory solution.
2	A value of 2 was assigned to those combinations with which a problem exists, but for which a remedy may be available. This is, the combination of component and parameter is deemed to be acceptable, with qualifications.
3	A value of 3 was assigned to those combinations which were deemed to be satisfactory; i.e., within the present state of the art.
U	A designation of U was made where the necessary information upon which to base a judgement was unavailable.
NA	Where a parameter was not applicable, the letters NA were used.

Following the Propellant Rating Chart is a discussion of the more serious problem areas (with ratings of 1 or 2) for each propellant type.

TABLE 1-1. PROPELLANT RATING CHART

LEGEND

1 POOR — NA - NOT APPLICABLE
2 FAIR — U - UNAVAILABLE INFORMATION (NO TEST DATA)
3 GOOD

PROPELLANT	COMPATIBILITY													VALVE TYPES					OVERALL PROBABLE RATING IN 10 YEARS
	METALS	CERAMICS	POLYMERS	WET LUBES	DRY LUBES	SHOCK SENSITIVITY	LUBRICITY	VISCOSITY	RADIATION TOLERANCE	EFFECTS OF LEAKAGE	CONTROL OF FLOW	SOFT SEATS	HARD SEATS	COMPONENT STERILIZATION[e]	REGULATORS	SHUTOFF	FLOW METERING	VENT (ZERO-G)	DISCONNECT	
EARTH STORABLES																				
FUELS																				
HYDRAZINE	3	3	3	2[c]	2	3	1	2	2	1-2	3	3	3	2-3	3	3	3	NA	3	3
MONOMETHYLHYDRAZINE		3	2	2[c]	1	3	U	3	2	1	3	U	U	2-3	3	3	3	NA	3	3
U-DIMETHYLHYDRAZINE	3	3	2	2[c]	1-2	3	1	3	2	1-2	3	3[a]	3	1-2	3	3	3	NA	3	3
AEROZINE-50	3	3	2	2[c]	1-2	3	1	2	2	1-2	3	3[a]	3	2-3	3	3	3	NA	3	3
PENTABORANE	3	2	2-3	2	3	3	U	3	3	1	3	2-3	2	U	3	2-3	2-3	2-3	3	2-3
OXIDIZERS																				
NITROGEN TETROXIDE	3	3	2	2	2	3	3	3	3	1-2	3	1-2	3	2-3	3	3	3	NA	3	3
SPACE STORABLES																				
FUELS																				
DIBORANE	3	2	2-3	2	3	3	U	3	3	1	3	2-3	2	U	2-3	2-3	2-3	2-3	3	2-3
HYBALINE A5																				
LPG[d]	3	3	3	2-3	2-3	3	2	3	2	2	3	3	3	U	3	1-2[b]	3	2	3	3
OXIDIZERS																				
CHLORINE TRIFLUORIDE	3	2	1-2	1	1	3	U	3	3	1	3	1-2	3	U	3	2[b]	3	NA	3	2-3
CHLORINE PENTAFLUORIDE	2-3	2	1-2	1	1	3	U	3	3	1	3	1-2	3	U	3	2[b]	3	NA	3	2-3
OXYGEN DIFLUORIDE	3	2	2	1	1	3	U	3	U	1-2	3	1	3	U	3	2[b]	3	2-3	3	2
PERCHLORYL FLUORIDE	3	2	2	1-2	1	3	U	2-3	U	1-2	3	2	3	U	3	2[b]	3	NA	3	2-3
NITROGEN TRIFLUORIDE	3	2	1-2	1	1	3	1-2	2-3	U	1	3	1-2	2-3	U	3	1[b]	1-2	1-2	2	2-3
NITRYL FLUORIDE	2-3	1-2	1	1	1	3	2	U	U	1	3	1-2	2-3	U	3	1[b]	1-2	1-2	2	2
TETRAFLUOROHYDRAZINE	3	2	1-2	1	1	3	2	3	U	1	3	1-2	2-3	U	3	1[b]	1-2	1-2	2	2
HARD CRYOGENICS																				
LIQUID FLUORINE	3	2	1-2	1	1	3	1-2	3	3	1	3	1-2	2-3	U	3	1[b]	1-2	1-2	2	2
LIQUID OXYGEN	3	3	2	1	1	3	2	3	3	2	3	2-3[a]	3	U	3	2[b]	3	2-3	2	3
LIQUID HYDROGEN	3	3	1-2	1	1	3	2	3	3	2	3	2-3[a]	3	U	3	1-2[b]	3	2-3	2	2-3
FLOX (80% LF_2, 20% O_2)	3	2	1-2	1	1	3	1-2	3	3	1	3	1-2	2-3	U	3	1[b]	1-2	1-2	2	2
GELS																				
LIQUID GELS	3	2	2	2	2	3	2	2	2	2	2	3[a]	3	1	U	1	2	NA	U	2
METALLIZED GELS	2	2	2	1-2	1-2	3	1	2-3	2	1	1	2	2	1	U	1	1	NA	U	2

a. THESE RATINGS, UNLIKE THOSE UNDER ORGANIC POLYMERS, WERE BASED ON THE USE OF A SPECIFIC POLYMERIC MATERIAL, IN MOST CASES TEFLON, FOR SOFT SEATS.

b. RATINGS BASED ON LEAKAGE CONTROL.

c. THESE RATINGS ARE BASED ON THE USE OF DUPONT FLUORINATED GREASE KRYTOX 240.

d. LIQUIFIED PETROLEUM GASES, METHANE, PROPANE, BUTENE.

e. 300°F, 60 HRS., 6 CYCLES.

EARTH STORABLE PROPELLANTS

FUELS

HYDRAZINE (N_2H_4)

Hydrazine is a clear liquid used as a high-energy propellant that is insensitive to mechanical shock or friction and exhibits excellent thermal stability at ambient temperatures. It is considered a hazardous propellant, however, due to its toxicity, reactivity, and flammability. Since it is thermodynamically unstable (i.e., a monopropellant), hydrazine will decompose under elevated temperatures when catalyzed by graphite or a metal oxide such as iron oxide or copper oxide, and will release considerable energy resulting in a possible explosion or fire. In addition, liquid hydrazine exerts sufficient vapor pressure above 100°F to form flammable air mixtures. Its freezing point is 35°F. Hydrazine is hygroscopic and readily forms flammable mixtures in air; therefore, a nitrogen blanket is required.

In assessing the compatibility of a material with hydrazine, the specific application for its use must be considered. Materials satisfactorily used with hydrazine where air oxidation of the surface can be prevented may not be satisfactory for service where prolonged exposure to air cannot be avoided. Factors to consider when selecting materials to use with hydrazine for any given exposure condition are: 1) corrosiveness of the material in contact with hydrazine and 2) the effect of the material and/or its corrosion products formed on the rate of decomposition of hydrazine.

These factors to be considered are particularly true for carbon steel, low-alloy steels, copper alloys, and molybdenum. From the corrosion standpoint, these metals are satisfactory for use in hydrazine; however, these metals and/or their oxides may catalyze hydrazine decomposition at elevated temperatures. At one time it was thought that 316 stainless (containing molybdenum) caused excessive hydrazine decomposition rates at elevated temperatures. However, it is now generally agreed that the

hazard at typical operating (<200°F) temperatures is no greater with 316 stainless than with any of the other 300 series stainless steels.

Table 1-2 lists those materials considered to be compatible with hydrazine for long-term application.

PHYSICAL PROPERTIES

Specific Gravity	1.00 (60°F)
Molecular Weight	32.048
Freezing Temperature °F	35.1
Normal Boiling Point °F	236.3
Critical Temperature °F	716
Critical Pressure psia	2131
Heat of Vaporization Btu/lb_m	540

Discussion of Problem Areas -
Hydrazine (N_2H_4)

Wet Lubes (2)* - Most wet lubes either wash off or are attacked by hydrazine. For limited use, some silicone lubricants and "Q-Seal," Quigley Company, have been used with fair results. A new fluorinated grease by DuPont, Krytox 240, appears to be compatible.

Dry Lubes (2) - Most dry film lubricants are attacked or removed by hydrazine. Electrofilm 1000G and Lubeco 2029-3 are partially compatible and can be used, although wear life after propellant exposure is somewhat reduced.

Lubricity (1) - Unsatisfactory lubricating performance was found for hydrazine in a series of low-load short duration ball bearing and gear tests at 24,600 rpm. The poor lubricity, resulting in degradation of the component metals surveyed, was attributed to its active solvent and reducing properties.

Viscosity (2) - The viscosity of hydrazine presents a problem only at low temperatures. The freezing point of commercial hydrazine is approximately 30°F, which is relatively high for operation under cold climatic conditions. Three methods of preventing N_2H_4 from freezing have been employed: 1) the addition of freezing point depressant, 2) insulation of container and components, and 3) insulation plus tracing with heat elements, steam, or hot water.

Radiation Tolerance (2) - Hydrazine, UDMH, and Aerozine 50, subjected to an irradiation dose of 1×10^9 erg/g, which is the maximum space radiation dose likely to be incurred in two years of operation in the Van Allen belts, showed that the composition of the propellants was not significantly affected. However, a pressure increase resulted, accompanied by the evolution of insoluble gases, due to slight decomposition. It is therefore recommended that tanks be designed to minimize this problem.

*Parenthetical enclosures refer to Propellant Rating Chart, Page 1-11.

Effects of Leakage (1-2)* – Anhydrous hydrazine is a flammable liquid, hence leakage may initiate a fire; it is hypergolic with most oxidizing agents and decomposes on contact with catalytic materials including iron rust. Vapors of hydrazine can be detonated by an electric spark or an open flame.

Since this propellant is a strong chemical reducing agent, leakage may result in malfunction of other elements in the system or injury to man. Prolonged exposure to this toxic material produces damage to the liver and kidneys and, to a lesser extent, anemia and lowering of blood sugar concentrations. The threshold value which has been adopted by the American Conference of Governmental Industrial Hygienists is 1 ppm.

*Parenthetical enclosures refer to Propellant Rating Chart, Page 1-11.

TABLE 1-2. HYDRAZINE (N_2H_4)

COMPATIBILITY OF MATERIALS FOR
LONG TERM APPLICATION (NOTE 1)

MATERIAL	TEST TEMP °F
ALUMINUM ALLOYS	
1100	140
2014	80
2017	160
2024	70
3003	80
4043	160
5052	80
5456	140
6061	160
6061-T6	110
6066	80
716	140
356	160
*356-T6	110
40E	75
Tens 50	-
STAINLESS STEEL	
410	80
416	200 (pits)
430	68
440C	80
302	80
304	140
316	200
317	80
321	140
347	200
17-4 PH	140
17-7 PH	75
AM 350	160
AM 355	160

*Reported noncompatible for period > 1 year based on limits of decomposition of hydrazine, see specific Reference 128.

HYDRAZINE (N_2H_4) (Continued)

MATERIALS	TEST TEMP °F
MISCELLANEOUS METALS	
Chromel A	80
Chromium Plating	70
Gold	75
Hastelloy C	125
Inconel	200
Inconel X	80
K-Monel	140
Monel	80
Nichrome Braze	80
Platinum	110
Silver	80
Silver Solder	75
Stellite 21	75
Tantalum	80
Tin	80
Titanium, A110AT	140
*Titanium, 6A1-4V	160
Zirconium	75
NON-METALS	
Butyl Rubber Compound 805-70	140
Butyl Rubber Compound 823-70 (Parco)	-
Butyl Rubber Compound B480 (Parker)	-
Butyl Rubber Compound 9257 (Precision)	-
Ethylene Propylene Co-polymer	110
Kel-F	80
Polyethylene	80
Teflon	140
Teflon Coatings	-

*Has been reported noncompatible for period >1 year at 110°F based on limits of decomposition of hydrazine, see specific Reference 128.

HYDRAZINE (N_2H_4) (Continued)

MATERIAL	TEST TEMP °F
NON-METALS	
Asbestos	80
Delanium	140
Glass	80
Polypropylene	-
SBR	75
Silicone Grease DC-11	-

Note 1. Metals listed above are rated compatible on a corrosion rate of less than 1 mil per year and the material does not cause decomposition, and is free from impact sensitivity. Non-metals are rated for satisfactory service for general use.

HYDRAZINE (N_2H_4) (Continued)

INCOMPATIBLE MATERIALS

INCOMPATIBLE MISCELLANEOUS METALS	INCOMPATIBLE NON-METALS
Cadmium	Buna-N Rubber
	Cellulose Acetate
Cobalt	Diallyl Phthalate
Lead	Epons
Magnesium	Kel-F 300 @140°F
	Kel-F @160°F
Zinc	Kel-F Grease @212°F
	Natural Rubber
Brass*	Neoprene Rubber
Bronze*	Nylon
Copper*	Mylar
Iron*	Polyester
Molybdenum*	Polyvinyl Alcohol
Mild Steel*	Polyvinyl Chloride
	Saran
6A-4V Ti (110°F, <1 year)**	Silastic LS-53
	Tygon

*The oxide of these metals act as catalysts for decomposition of hydrazine at elevated temperatures.

**Outside limit for decomposition rate of hydrazine, see specific Reference 128.

MONOMETHYLHYDRAZINE (CH_3NHNH_2)

Monomethylhydrazine (MMH) is a clear, water white liquid with a strong amine odor detectable in concentrations of 1 to 3 ppm. It is a fairly volatile liquid; the vapor pressure, 0.96 psia at 77°F, is higher than that of hydrazine and hence creates a more hazardous health problem than hydrazine. The maximum allowable concentration of MMH vapor in air has not been established, but it has been suggested that it be set within 0.1 and 0.5 ppm.

Liquid MMH is not sensitive to impact or friction and is more stable than hydrazine under conditions of mild heating. The flammibility characteristics of MMH with air are close to those of hydrazine and UDMH; consequently it should be maintained under a nitrogen blanket at all times. MMH must be stored away from any oxidizers and from possible sources of ignition. All metallic equipment employed for storage and handling of MMH requires grounding to prevent an accumulation of static charge.

An extensive compilation of compatibility data for metals and non-metals is not available. Due to the similarity in catalytic oxidation and chemical activity for MMH and hydrazine, those metals found satisfactory for hydrazine should suffice for MMH. In general, monomethyldhyrazine attacks organic materials more readily than does hydrazine. Only short-term studies on a selected few plastics have been reported; no long-term compatibility tests have been done. Table 1-3 lists the materials which have been found to be satisfactory for use in the storage and handling of MMH.

PHYSICAL PROPERTIES

Molecular Weight	46.075
Freezing Temperature °F	-63
Normal Boiling Point °F	189
Critical Temperature °F	609
Critical Pressure psia	1195
Heat of Vaporization Btu/lb_m	377

Discussion of Problem Areas -

Monomethylhydrazine

Organic Polymers (2)* - In general, monomethylhydrazine attacks organic materials more readily than does hydrazine. Materials satisfactory for limited use include Teflon, some silicone rubbers and high density polyethylene.

Wet and Dry Lubes (2) - Because monomethylhydrazine is a better solvent than UDMH and N_2H_4, it also has attendant undesirable lubricant and "wash-out" effects. DuPont's Krytox 240 grease is compatible. Electrofilm 2406 and 1000G dry film lubricants have shown an ability to withstand attack. However, lubricity after exposure is undetermined. Cico 200-029-3 dry film lubricant has shown an increase in wear life after 72 hours exposure to monomethylhydrazine.

Radiation Tolerance (2) - This rating was made by analogy to hydrazine and UDMH, which have very similar chemical structure and physical and chemical properties.

Effects of Leakage (1) - Monomethylhydrazine is somewhat more toxic than UDMH or hydrazine; its flammability characteristics are similar. MMH vapors detonate on ignition by static sparking. Iron rust promotes the catalytic decomposition, resulting in spontaneous ignition. For effects of space vacuum, see the discussed effects of leakage for hydrazine.

*Parenthetical enclosures refer to the Propellant Rating Chart, Page 1-11.

TABLE 1-3. MONOMETHYLHYDRAZINE

COMPATIBILITY OF MATERIALS
FOR SHORT TERM USE[a]

MATERIAL	TEMPERATURE
ALUMINUM ALLOYS	
3003	
5052	
5154	
6061-S	Satisfactory below 160°F
MISCELLANEOUS ALLOYS	
Titanium 6A1-4V	
Columbium C 103	
STEELS	
303 Stainless Steels	
304 Stainless Steels	
321 Stainless Steels	
347 Stainless Steels	
17-7 PH Stainless Steels	
4130[b]	Satisfactory below 160°F
BRAZES	
Aerobraze-T	
82 Au-18 Ni Braze Alloy	
PLASTICS AND ELASTOMERS	
Natural Rubber	Intermediate[d] below 160°F, 1 wk
Neoprene	Intermediate[d] below 160°F, 1 wk
Polyethylene (high density)	Good[c] below 160°F, 1 wk
Silicone Rubber	Intermediate[d] below 160°F, 1 wk
Teflon	Intermediate[d] below 160°F, 1 wk
Some unplasticized trichlorofluoroethylenes	
Butyl Rubber	Below 95°F

a Two to four weeks.
b Very susceptible to rusting.
c Negligible weight change (0.5%); no change in elasticity.
d Moderate weight change (0.5 - 2.5%); change in elasticity of 25-40%.

UNSYMMETRICAL DIMETHYLHYDRAZINE $(CH_3)_2NNH_2$

UDMH is a derivative of hydrazine and is a moderately toxic, shock insensitive, storable liquid propellant. It exhibits excellent thermal stability and resistance to catalytic breakdown. It has a lower freezing point and higher boiling point than hydrazine.

Due to an extremely wide flammable range in air and the possibility that explosive vapor-air mixtures may be found above the liquid, UDMH should not be exposed to open air. Instead, it should be stored in a closed container under a nitrogen blanket.

At the present time test results imply that lubricants which are compatible for use with UDMH are still in the development stage. Lubricants such as APS C-407, Parkerlube 6PB, Molykote, and Peraline 12-4 may cause decomposition, while petroleum and silicone greases which do not react but are dissolved by the UDMH.

Table 1-4 lists those materials which are considered to be compatible with UDMH for long-term application.

PHYSICAL PROPERTIES

Specific Gravity	0.785 (60°F)
Molecular Weight	60.078
Freezing Temperature °F	-72
Normal Boiling Point °F	146
Critical Temperature °F	480
Critical Pressure psia	880
Heat of Vaporization Btu/lb_m	250.7

Discussion of Problem Areas -

Unsymmetrical Dimethylhydrazine (UDMH)

Organic Polymers (2)* - In view of the variable nature of the service in which organic polymeric materials might be employed, it is difficult to be specific regarding their performance. Because of the excellent solvent properties of UDMH, most polymeric materials prove unsatisfactory. Numerous plastics and rubbers are rated "good" (suitable for repeated short-term exposure). Of the references cited, all indicated that Teflon was not attacked by UDMH and rated it as suitable for long-term storage or exposure.

Wet and Dry Lubes (2) - Because of the excellent solvent properties of UDMH, most lubricants are incompatible. Several lubricants, litharge, glycerine paste, X-Pando, and Q-Seal, are compatible and have been employed for pipe threads and other similar applications involving minimum contact with UDMH. Petroleum and silicone greases do not react, however, they tend to "wash-out" under dynamic conditions. DuPont's fluorinated grease, Krytox 240 is compatible.

Lubricity (1) - UDMH was found to have unsatisfactory lubricating properties when subjected to bearing and gear tests. The performance was thought to be related to the excellent solvent and reducing properties of UDMH.

Radiation Tolerance (2) - See hydrazine.

Effects of Leakage (2) - Being chemically similar to hydrazine, the same hazards are encountered as with that material. The maximum allowable concentration is somewhat less (0.5 ppm) than hydrazine. It is flammable in air, hypergolic in the presence of oxidizers; its excellent solvent properties may cause malfunction of components constructed of incompatible organic plastics with which it may come in contact. For space conditions, see the discussion on effects of leakage for hydrazine.

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*Parenthetical enclosures refer to Propellant Rating Chart, Page 1-11.

TABLE 1-4. UNSYMMETRICAL DIMETHYLHYDRAZINE (UDMH)

COMPATIBILITY OF MATERIALS FOR
LONG TERM APPLICATIONS (NOTE 1)

MATERIALS	TEST TEMP °F
ALUMINUM ALLOYS[a]	
1100	160
1100-H14	145
1260-H14	145
2014	140
2017	75
2024	75
2024-T3	145
3003	86
3003-H14	145
3004-H34	145
5052	160
5052-H34	145
5086	85
5086-H34	145
5154-H34	145
5456	140
6061	160
6061-T6	145
6063-T6	145
7075	160
7075-T6	145
356	160
356-T6	85
43	145

a Aluminum is attacked by UDMH if water is present, with the attack being directly proportional to the amount of water present.

UNSYMMETRICAL DIMETHYLHYDRAZINE (UDMH) (Continued)

MATERIALS	TEST TEMP °F
STAINLESS STEEL	
302	160
303	160
304	160
316	140
321	160
347	160
410	160
416	250
422	145
17-7 PH	160
Carpenter 20	140
PH15-7 Mo	85
A286	85
AM350	
AM355 CRT	100
17-4 PH Cond H925	
17-4 PH Cond H1151	
MISCELLANEOUS METALS	
Copper	145
Hastelloy (B, C, X, F)	145
Haynes Alloy 25	140
Inconel	140
Magnesium Alloy AZ-31B-O	85
Magnesium Alloy AZ-31B, AZ-61A	130
Magnesium Alloy AZ-92-F	85
Mild Steel	140
4130 Steel	85
Monel	140
Nickel	140

UNSYMMETRICAL DIMETHYLHYDRAZINE (UDMH) (Continued)

MATERIALS	TEST TEMP °F
MISCELLANEOUS METALS (Cont.)	
Tantalum	140
Titanium Alloy 6Al-4V	
Titanium A-55 (Commercially Pure)	145
Titanium Alloy B-120VCA	145
Titanium Alloy C-120AV	160
Columbium C 103	
PLASTICS AND ELASTOMERS	
Butyl Rubber	140
Kel-F (Unplasticized)	140
Nylon	130
Polyethylene	80
Teflon (FEP)	160
Teflon (TFE)	160
MISCELLANEOUS MATERIALS	
Delanium	75
Glass Pyrex	160
Graphitar No. 2	140
Graphite	75

Note 1: Materials listed above are rated compatible based on a corrosion rate of less than 1 mil per year and the material does not cause decomposition, and is free from impact sensitivity. Non-metals are rated for satisfactory service for general use.

AEROZINE-50 (50% HYDRAZINE/50% UDMH)

The storable fuel blend of a nominal 50 percent by weight of hydrazine (N_2H_4) and 50 percent by weight of unsymmetrical dimethylhydrazine (UDMH) is a hygroscopic (readily capable of absorbing moisture) liquid which is insensitive to mechanical shock but flammable in both liquid and vapor states. When combined, there is a definite tendency for each to dissolve in the other. Since the vapor above the fuel blend at 72°F is predominantly UDMH, the flammability hazards of the mixture are the same as for UDMH. Explosion hazards can be minimized, however, by maintaining the fuel in closed systems.

Most common metals which might be used for valve construction, with the exception of the magnesium and copper alloys, are compatible with the 50/50 fuel blend providing they are clean. Care should be exercised when using ferrous alloys because of the possible catalytic decomposition of the fuel blend due to rust. Titanium alloy 6AL-4V has been reported non-compatible based on hydrazine decomposition rate limits (see specific Reference 128.

Table 1-5 lists those materials which are considered to be compatible with the 50/50 fuel blend for long term application.

PHYSICAL PROPERTIES

Molecular Weight	41.797
Freezing Temperature °F	18
Normal Boiling Point °F	170
Critical Temperature °F	634
Critical Pressure psia	1696
Heat of Vaporization Btu/lb_m	425.8

Discussion of Problem Areas -
Aerozine-50 (N_2H_4 and UDMH)

Organic Polymers (2)* - Most organic polymers either dissolve or deteriorate in the presence of Aerozine-50. Teflon has proved most successful for some uses; butyl rubbers are being used for most dynamic seals.

Wet Lubes (2) - Certain silicone-base greases, polyglycol oils, and powdered Teflon have been used for limited service. The fluorolubes react; many dissolve. DuPont's fluorinated grease, Krytox 240 is compatible.

Dry Lubes (1-2) - Graphite has been used, but found susceptible to washing out under dynamic conditions. Electrofilm 2406 and 1000 have shown resistance to propellant attack. However, lubricity after exposure is unknown.

Lubricity (1) - Being a mixture of hydrazine and UDMH, Aerozine-50 would have properties similar to the two components.

Viscosity (2) - Because of the high freezing temperature (18°F) of the Aerozine-50 mixture and the rapid increase in viscosity as this temperature is approached, it is desirable to maintain fuel temperature well above this point to insure proper flow characteristics.

Radiation Tolerance (2) - See hydrazine.

Effects of Leakage (1-2) - The leakage effects will be similar to those discussed for the components of the fuel blend.

*Parenthetical enclosures refer to Propellant Rating Chart, Page 1-11.

TABLE 1-5. AEROZINE-50 (50% HYDRAZINE/50% UDMH)

COMPATIBILITY OF MATERIALS FOR
LONG TERM APPLICATION

MATERIAL	TEST TEMP °F
ALUMINUM ALLOYS	
1100	55-60
2014-T4	55-60
*2014-T6	160
*2024-T6	160
2219-T81	55-60
3003-H14	150
5086-H36	160
5254-F	160
5456-H24	55-60
5456-H321	160
6061-T6	160
6066	160
*7075-T6	160
356	160
Tens 50	160
STAINLESS STEEL	
303	160
304L	
*316	160
321	160
347	160
PH15-7 Mo (Cond. A)	160
*17-4 PH	160
17-4 PH (Cond. A)	160
*AM355 (Cond. H)	160
*AM350 SCT	160
*410H and T	160
440C	160

*Disagreement exists among authorities as to acceptability.

MATERIALS	TEST TEMP °F
OTHER METALS	
*Anodize Coatings on Aluminum	160
Berlyco 25	160
Cadmium Plate	60
Columbium C 103	
Non-porous Chromium Plating	55-60
Gold Plate	160
Monel	80
Nickel	160
Non-porous Electrolytic Nickel Plating	55-60
*Electroless Nickel Plating	160
Silver	55-60
Silver Solder	60
Stellite 6K	160
*Stellite 21	160
Stellite 25	160
A286 Steel (rust free)	55-60
*1020 Steel (rust free)	55-60
4130 Steel (rust free)	55-60
Ti Alloy A110-AT	160
Ti Alloy C 120AV	160
Ti Alloy B 120VCA	55-60
**Titanium 6Al-4V	110
Tin	55-60
Titanium Carbide (Ni Binder)	160
Tungsten Carbide	160
PLASTICS AND ELASTOMERS	
Enjay 035	80
Fluorobestos filled with Asbestos	55-60
Fluorogreen	55-60

*Disagreement exists between authorities as to acceptability.
**Reported noncompatible based on limits of decomposition rate of hydrazine, see specific Reference 128.

AEROZINE-50 (Continued)

MATERIALS	TEST TEMP °F
PLASTICS AND ELASTOMERS (Cont.)	
Hadbar SB800-71 Rubber	160
Kel-F 300 (15% Glass Filled)	75
Kel-F 300 (Unfilled)	75
Parker B496-7 Rubber	160
Low-density Polyethylene	60
Polypropylene	160
Precision Rubber 9257, 940, X559	80
Teflon (FEP)	70-80
Teflon (TFE)	70-80
Teflon filled with Graphite	55-60
Teflon filled with Molydisulfide	55-60
Teflon filled with Asbestos	55-60
Zytel 31 Nylon	70-80
Zytel 101 Nylon	60
LUBRICANTS AND GRAPHITE	
Flake Graphite	80
Graphitar 39	70-80
Graphitar 84	70-80
Graphitar 86	160
Microseal 100-1 (dry lube)	80
National Carbon CCP-72	160
Purebon P3N	160
Reddy Lube 100	80
Reddy Lube 200	80
Silicone DC 11	80
Water Glass Graphite	80
Krytox 240	80

AEROZINE-50 (Continued)

MATERIALS	TEST TEMP °F
CERAMICS	
Rockflux	75
Sauereisen P-1	60
Sauereisen 31	60
Temporall 1500	60
ADHESIVES	
Epon 422	80

PENTABORANE (B_2H_9)

Pentaborane is a high energy fuel which is an extremely hazardous pyrophoric compound which is insensitive to mechanical shock and in an inert atmosphere, exhibits satisfactory (to 77°F) thermal stability. It exhibits hypergolicity with the high-energy oxidizers, and behaves as a strong reducing agent in oxidation-reduction reactions.

The boranes have a pungent, sickeningly sweet odor, and are toxic to a high degree. Toxic concentrations are reached before any odor can be detected and special detectors must be used. Any substance which will function as a potential oxidizer will react with the boranes. Materials such as water, air, metal oxides, and reducible organic compounds are in this category. For this reason, considerable care should be exercised in the selection of materials to be used with pentaborane, so as to avoid use of any organic compounds containing a reducible functional group. Teflon, Viton, Kel-F, and Fluorosilica rubber are among the compatible polymers.

Organic materials such as gaskets, lubricants, and seals must be chemically inert if they are to be used. High-porosity castings and gaskets should be avoided. Because of the ability of the boranes to reduce some metal oxides, welded joints should be avoided in pipe constructions. To date, no metals are known to be incompatible with pentaborane at ordinary room temperatures and atmospheric pressures. Pentaborane forms shock-sensitive mixtures with many highly chlorinated organic compounds such as carbon tetrachloride or trichloroethylene and with organic compounds containing reactive carbonyl groups such as acetone, other keytones and aldehydes. Thus, strict housekeeping rules and thorough solvent removal procedures must be employed when cleaning components such as valves, etc., in propellant systems using pentaborane.

Table 1-6 lists those materials which are considered to be compatible with the pentaborane for long-term application.

PHYSICAL PROPERTIES

Molecular Weight	63.17
Freezing Temperature °F	-52
Normal Boiling Point °F	136
Critical Temperature °F	435
Critical Pressure psia	557
Heat of Vaporization Btu/lb_m	219
Density, gm/cc	0.643 (32)

Discussion of Problem Areas -
Pentaborane (B_5H_9)

Ceramics (2)* - Because of their strong reducing properties, pentaboranes will reduce some metal oxides and also precipitate some heavy metals from solutions of their salts.

Wet Lubes (2) - A number of lubricants are satisfactory for short-term service; however, pentaborane, being soluble in these lubricants, presents problems of cleaning, disposal, and "wash-out" of lubricant from components. Generally, non-lubricated valve designs acceptable for use with other toxic and corrosive liquids may be used successfully with the boranes.

Effects of Leakage (1) - The toxicity of the boranes, with a tentative threshold limit of 0.005 ppm, would constitute a severe hazard to humans in the event of leakage. The pyrophoricity of pentaborane in air has been a controversial subject; however, it is generally agreed pentaborane must be treated as if it were spontaneously flammable in air under most conditions. For leakage in space, see the discussion on effects of leakage for hydrazine.

Hard Seats (2) - Because of the necessity of eliminating all leakage, soft seat materials compatible with the boranes are recommended. Particle

*Parenthetical enclosures refer to Propellant Rating Chart, Page 1-11.

migration occurring where valve parts rub on plastic seals may cause problems of seal life, plugging or opening and fouling up close tolerance fits.

TABLE 1-6. PENTABORANE

COMPATIBILITY OF MATERIALS FOR LONG TERM APPLICATIONS

MATERIAL	TEMPERATURE °F
ALUMINUM ALLOYS	
2024-T3	75
3003-H14	75
5052-S	75
6061-T6	75
7075-T6	75
356-T6	75
Cadmium Coated Aluminum	75
Chromated Aluminum	75
STAINLESS STEELS	
302	75
304	75
321	75
347	75
OTHER METALS	
Brass	75
Cadmium Plated Steel	75
Copper	75
Hastelloy No. X-1258	75
Iron	75
K-Monel	75
Magnesium Alloy, AZ63A	
Magnesium Alloy, AZ318	

PENTABORANE (Continued)

MATERIAL	TEMPERATURE °F
OTHER METALS (Cont.)	
Monel, Soft, M-8330-B	
Nichrome "V"	75
Steel	75
Titanium Alloy C-110M	75
Titanium Alloy C-130AM	75
NON-METALS	
Fluoroflex T	75
Fluorosilicone Rubber	75
Graphitar No. 39	75
Graphite Impregnated Asbestos	75
Kel-F No. 5500	75
Kel-F & Glass Cloth	75
Kel-F & Glass Yarn	75
Molybdenum Disulfide	75
Pure Carbons	75
Rockwell Nordstrom Lube No. 921	75
Teflon	75
Viton	75
Viton A	75

Note 1: Materials listed above are rated compatible based on corrosion rate of less than 1 mil per year and the material does not cause decomposition, and is free from impact sensitivity. Non-metals are rated for satisfactory service for general use.

- PENTABORANE

INCOMPATIBLE MATERIALS

INCOMPATIBLE NON-METALS	INCOMPATIBLE LUBRICANTS
Foamglass	Rockwell Nordstrom Lube 356
Dow Corning R7002 Foam	Rockwell Nordstrom Lube 833
Dow Corning R7003 Foam	Rockwell Nordstrom Lube 860
Napco F10 Foam	Rockwell Nordstrom Lube 852-S
Napco B49	Rockwell Nordstrom Lube P-21
Natural Rubber	Rockwell Nordstrom Lube P-55
Nitrile Rubber on Nylon	Rockwell Nordstrom Lube 942-S
Dow Corning 9283 Rubber	
Saran	
Nylon	
Mylar	
Tygon	
Rubatex G-2027 N	
Rubatex R-103 J	
Fiberfrax No. XSW	
Fiberfrax No. SIF	
Dow Corning Silastic 80-24-480	
Garlock Silastic 250	

OXIDIZERS

NITROGEN TETROXIDE (NTO) (N_2O_4)

Nitrogen tetroxide is a highly reactive, toxic oxidizer, insensitive to all types of mechanical shock and impact. It is a dense brown or green liquid, depending on the NO content, and although it is nonflammable itself, it will support combustion and will react hypergolically upon contact with certain high-energy fuels such as the hydrazines. N_2O_4 can cause spontaneous ignition with common materials such as leather and wood. The fumes are extremely toxic. Nitrogen tetroxide is used as a storable propellant oxidizer and is used in the Titan II missile and many spacecraft propulsion systems.

Dry nitrogen tetroxide is compatible with many metals and alloys used in space vehicle construction. However, water contamination present in the nitrogen tetroxide causes the formation of nitric acid, which is corrosive to many metals; therefore, materials selected for use in N_2O_4 should be compatible with nitric acid as well. Gold and a few types of stainless steel have been satisfactory as materials in nitric acid storage containers and so should be best for long-term N_2O_4 containment.

In general, aluminum alloys and stainless steels are most suitable for use as materials in contact with dry nitrogen tetroxide. The resistance to corrosion exhibited by the various aluminum alloys is a function of water content in the nitrogen tetroxide and the aluminum content of the alloy in question. As the water content in the nitrogen tetroxide exceeds 0.3 percent, highly alloyed aluminum (e.g., 7075 Aluminum Alloy) shows a sharp increase in corrosion rates as contrasted by the purer aluminum alloys (e.g., 1100 Aluminum Alloy), whose increase in corrosion rate is much less pronounced. For stainless steel, however, the corrosion rate in nitrogen tetroxide varies directly with water content.

Stress corrosion of titanium tanks has been experienced with the use of Mil Spec grade N_2O_4 (MIL-P-26539A). Addition of small amounts of NO (>1.0%)

in order to scavenge the dissolved oxygen has given dramatic evidence of reducing the incidence of stress corrosion in titanium tanks containing NTO. Shot peening the inside of titanium tanks in order to produce a surface under compression also has been effective in reducing corrosion by brown NTO. Thus, the true nature of the factors producing stress corrosion in titanium by NTO are still incompletely resolved. Copper, magnesium and nickel alloys are not recommended for use because of their poor corrosive resistance to nitric acid.

The chloride content of NTO may also give rise to pitting corrosion, which is a particularly serious matter with respect to very thin walled containers and/or bellows which must have long-term service life. This, coupled with the demonstrated problems of nitric acid production from moisture present and the uncertain role of O_2 in NTO, clearly dictate that the aerospace designer should consider his choice of materials carefully in order to minimize failure due to materials incompatibility.

Most monmetallic materials show poor resistance to nitrogen tetroxide and are considered unsatisfactory for use. Reaction of nitrogen tetroxide with non-metals can result in decomposition of the materials, causing degradation or complete destruction, or it can alter the physical properties such as volume and/or hardness of the material. In certain cases, this reaction can be advantageous as in the case of butyl rubber seals. Reaction of the butyl rubber with NTO results in tackiness and swelling which seems to augment the sealing characteristics of the material. This type of seal has been reported successful in field service for over one year. The propellant may also be affected in its physical characteristics. Of all the plastics available for use, Teflon and Teflon products exhibit the best resistance to nitrogen tetroxide; however, nitrogen tetroxide permeates and is absorbed by Teflon. Results from permeability tests conducted show that the permeability rate for Teflon TFE is three times greater than Teflon FEP. Under certain conditions, Teflon in conjunction with NTO has caused increased corrosion rates. This may be due to the water content of NTO; however,

no long-term storage data are available. Recently, the cyclized polybutadienes (HYSTL) and some of the nitroso copolymers (CF_3NO/C_2F_4), and terpolymers ($CF_3NO/C_6F_5NO/C_2F_4$) have shown promise as organic materials for use with NTO.

Another method of circumventing seal problems with NTO has been to design the O-ring groove such that less than 2% seal exposure is allowed. The swelling of the polymer then closes the gap and does not allow further interaction of the seal with the NTO. It has been claimed that over ten months storage life without leaks has been accomplished by this procedure.

Most lubricants in contact with nitrogen tetroxide are either dissolved and washed off or undergo a substantial change in hardness. DuPont's fluorinated grease, Krytox 240 and several dry lubricants such as Molykote Z, Drilube 703, and Electrofilm 66-C have been rated as compatible with nitrogen tetroxide. Microseal 100-1 is rated as compatible with nitrogen tetroxide and does not undergo any physical changes.

The formation of a gelatinous material has been reported and occurs during high velocity flow on N_2O_4 through small clearances. Investigation of this phenomena is being carried out at several agencies and companies. The formation of the clogging material seems to be correlatible to various impurities in N_2O_4 introduced either during the manufacture, storage, or conditioning of the oxidizer. The materials that appear to be responsible are metal-N_2O_4 reaction products and, possibly, organic species formed subsequent to the actual usage of the N_2O_4. A more comprehensive discussion of the problem is found on page 2-1 and Reference 1 of that section.

Table 1-7 lists those materials which are considered to be compatible with nitrogen tetroxide for long-term application. It should be noted that temperatures, temperature ranges and percent of water contamination are

parameters of conducted tests and are not necessarily temperature limits or moisture content limits.

PHYSICAL PROPERTIES

Specific Gravity	1.49 (60°F)
Molecular Weight	92.016
Freezing Temperature °F	11.8
Normal Boiling Point °F	70
Critical Temperature °F	316
Critical Pressure psia	1470
Heat of Vaporization Btu/lb_m	178.2

Discussion of Problem Areas -
Nitrogen Tetroxide (N_2O_4)

Organic Polymers (2)* - No completely satisfactory non-metallic material has yet been found for use as valve seats. Most organic polymers have some disadvantages, principally that of swelling when exposed to N_2O_4. Polymers of promise have not been fully characterized as yet in NTO service.

Wet Lubes (2) - Most lubricants absorb N_2O_4, rendering them useless. Certain silicone greases have limited use because they tend to absorb N_2O_4 slowly. DuPont's fluorinated grease, Krytox 240 has been rated compatible.

Dry Lubes (2) - A number of dry lubricants, including graphite and molybdenum disulfide, show good compatibility, but tend to wash out under flow conditions.

Effects of Leakage (1) - N_2O_4 is a highly toxic substance and thus is classified as a poison on ICC regulations. The maximum allowable concentration of 5 ppm in air is accepted by the American Conference of Government Hygienists. Because of its corrosive nature and reaction with, or absorption in organic materials, adjacent components may easily be affected by N_2O_4 leakage. The hypergolic nature of N_2O_4 with many fuels constitutes a potential fire problem if leakage allows the two propellants to mix. Effects of leakage in space are discussed under the propellant hydrazine.

Soft Seats (1-2) - A limited number of non-metallic materials are satisfactory for short-term use, but it is recommended that polymeric seals be avoided whenever possible. Teflon and Kel-F are the more resistant plastic materials. Teflon, while compatible with N_2O_4, absorbs N_2O_4 vapors slowly. The resultant swelling may result in component malfunction.

*Parenthetical enclosures refer to Propellant Rating Chart, Page 1-11

TABLE 1-7. NITROGEN TETROXIDE

COMPATIBILITY OF MATERIALS FOR
LONG TERM APPLICATION

MATERIAL	TEST TEMP °F	% MOISTURE CONTENT
ALUMINUM ALLOYS		
1060	80	0.2 to 1.0
1100	60	0.3
1100-0	60	0.2 to 1.0
2014-T6	60	0.2 to 1.0
2014-T6 (Hardas Anodize)	60	
2014-T6 (H_2SO_4 Anodize)	65	
2014-T6 (Iridite)	60	
2014-T6 (Welded)		
2024	140	0.2 to 1.0
2024-0	150	
2219-T6	60	
2219-T81	60	0.2 to 1.0
3003-H14	150	0.6
4043	80	
5052	130	0.2 to 1.0
5086-H34	165	
5086-H36	65	
5254-F	65	
5456	60	
5456 H-24	60	0.2 to 1.0
5456 H-24 (Iridite)	60	
5456 H 321	65	0.2 to 1.0
6061	130	
6061-T6	130	0.2 to 1.0
6061-T6 (Welded)	65	
6066	65	
7075	60	
7075-0	150	
7075-T6	150	

NITROGEN TETROXIDE (Continued)

MATERIAL	TEST TEMP °F	% MOISTURE CONTENT
ALUMINUM ALLOYS (Cont.)		
7075-T6	60	0.2 to 1.0
356	80	
356-T6 (See Incompatible Listing)	80	0.2 to 1.0
Tens 50	65	
STAINLESS STEELS		
410	110	
416	110	
430	110	
440C	110	
302	100	
303	80	0.2 to 1.0
304	140	0.2 to 1.0
304L	165	3.2
316	65	
321 (Incl. Welded)	60	3.0
347 (Incl. Welded)	100	10.0
17-4PH (Cond. A)	65	
17-4PH (H1000)	100	0.3
17-4PH	65	3.0
17-7PH (TH950)	100	
17-7PH (RH950)	100	
AM-350 (Annealed)	100	10.0
AM-355 (Cond. H)	100	
MISCELLANEOUS METALS		
Chromium Plate	60	
Haynes Stellite 1	100	
Haynes Stellite 12	100	
Haynes Stellite 6K	65	
Haynes Stellite 21	65	
Haynes Stellite 25		

NITROGEN TETROXIDE (Continued)

MATERIAL	TEST TEMP °F	% MOISTURE CONTENT
MISCELLANEOUS METALS (Cont.)		
Haynes Stellite 93	100	
Gold	75	
Gold Plate	60	
Cast Iron	80	
Carbon Steel	80	
Mild Steel	140	
1020 Steel	130	
A-285 (Grade C)	165	3.2
8630 Steel	140	
A286 (Annealed) Steel	100	
A286 (Aged)	60	
PH15-7 Mo (Cond. A)	165	3.2
Magnesium, 100A	60	
Magnesium, HM21A-T8	60	
Nickel Electroplate	60	
Electroless Nickel Plate	100	
Inconel	65	
Monel	65	
Ni-Span-C	60	
Inconel X	75	
Platinum	75	
718 Braze 6061-T6A1	65	
Pure Tin Solder on 303SS	65	
Easy Flo Braze on 347SS	65	
Tantalum	75	
Tin	80	
Columbium	75	

NITROGEN TETROXIDE (Continued)

MATERIAL	TEST TEMP °F	% MOISTURE CONTENT
NON-METALS		
Microseal 100-1 on 2014-T6A1	100	
Teflon TFE	75	
Teflon FEP	160	0.2 to 1.0
Teflon Graphite	75	
Teflon MoS_2	75	
Teflon Asbestos	75	
Teflon Glass Filled	80	
Alcar 191	67	
Armalon 7700	75	
Armalon 7700B	75	
Fluorobestos	60	
Fluogreen	60	
Genetron GCX-3B	80	
Genetron XE-2B	65	
Kynar	80	
Raythene N. (Irradiated)	65	
Tedlar	67	
LUBRICANTS		0.2
XC 150	65	
Molykote Z	60	
Microseal 100-1	67	
Lox Safe	80	
Flake Graphite	80	
Graphitar 2, 14, 39, 50, 86	67	
CCP-72		
Fluorolube MG6DO	80	
Fluoroethane G	80	
Krytox 240	80	

NITROGEN TETROXIDE (Continued)

MATERIAL	TEST TEMP °F	% MOISTURE CONTENT
SEALANTS AND POTTING COMPOUNDS		0.2
Reddy Lube 100	160	
Reddy Lube 200	160	
Waterglass-Graphite	67	
Oxylube Sealant	80	
Teflon Tape (Unsintered)	80	
Crystal M&CF	60	
4-3	60	
Sauereisen P-1	60	
Proseal 333	60	

NITROGEN TETROXIDE

INCOMPATIBLE MATERIALS - Note 1

INCOMPATIBLE METALS

Cadmium
Lead
356-T6 Aluminum Alloy (110°F, 1.9 yr)
Copper
K-Monel
Silver
Sintered Molybdenum
Zinc
Zirconium
Cobalt
Hastelloy B (110°F)
Magnesium A231C (110°F)

INCOMPATIBLE NON-METALS

ELASTOMERS

Natural Rubber
Butyl Rubber
Buna-N
Neoprene
Viton
Chloroprene
Ethylene Propylene
Silicones
Kel-F
Hypalon
Polyurethane

INCOMPATIBLE NON-METALS

PLASTICS

Kel-F
Polyethylene
Nylon
Mylar
Polyvinylidene Chloride
Acrylics
H-Film
Polypropylene
Silicone Laminates
Epoxy Laminates
Phenalic Laminates
Polyester Laminates
Polyvinyl Chloride
Epon Resins
Acetal Resins
Vinyl

NITROGEN TETROXIDE

INCOMPATIBLE MATERIALS Note 1

INCOMPATIBLE NON-METALS

LUBRICANTS

- DC 11
- DC 33
- DC 510
- DC 550
- Molykote M-8800
- Molykote X-106
- Drilube 7
- Drilube 1
- Surfkote N-1284
- Rayco 30
- Electrofilm 66C
- Johns Manville No. 60

INCOMPATIBLE SEALANTS AND POTTING COMPOUNDS

- Polysulfides
- RTV Silicones
- Epon Resins
- Polyesters
- Polyurethanes

Note 1 - Plastics, elastomers and sealants are generally listed by chemical family. While not all commercial products have been tested, it has generally been determined that these chemical families are incompatible. Lubricants included are rated on basis of wash-out tendencies or failure to maintain lubricity after propellant exposure.

CORROSION OF MATERIALS WITH IMPURE N_2O_4

TRW Systems performed corrosion testing using engineering materials at elevated temperatures with impure N_2O_4 for NASA (General Reference No. 18). It was the intent of the NASA program to enhance corrosion, not suppress it, for purposes of determining the effect of corrosion products on contaminating the N_2O_4. However, this information and test data generated is valuable, since it represents the only known matrix testing done showing the effects of impurities in the propellant on corrosion. The work also included a different rating analysis on reporting corrosion not generally used by investigators. The test specimens were unstressed samples of 6061-T6 Aluminum, 347 Stainless Steel and Ti-6Al-4V Alloy subjected to one and four month durations at 165°F. The specimens measured nominal 0.025" thickness x 3/4" x 4" long and were placed in glass capsules containing the N_2O_4 and sealed. The impurities individually added to the N_2O_4 are listed as follows:

ADDED IMPURITY	PRE-STORAGE CONCENTRATION, % w/w
Chlorine (Cl_2)	0.10
Water (H_2O)	0.91
Oxygen (O_2)	0.04
Nitrosyl Chloride (NOCl)	0.025
Nitrosyl Chloride + O_2 (NOCl + O_2)	0.054 NOCl + 0.050 O_2

The effects of the selected impurities in the corrosivity of N_2O_4 showed no significant increase in dissolved metal content with time. Of all the impurities, water resulted in the greatest increase in corrosivity. Tables 1-8, 1-9, and 1-10, present a visual description of the appearance of the one and four month specimens. Tables 1-12 through 1-14 lists the results of the corrosion testing for all three metals. Table 1-11 gives the definitions of the rating analysis used in the corrosion results of Tables 1-12 through 1-14. The rating analysis is taken from Champion, General Reference 1.

6061-T6 Aluminum

The water contaminated N_2O_4 caused the greatest weight change in the aluminum and also caused the greatest structural damage to the metal. A significant decrease in water content after the four month storage period is noted. The samples were covered with a very thick, white coating which was easily removed by washing. Greatest damage appeared to be concentrated in the rolling marks left in the metal during sheet fabrication. Oxygen and O_2/NOCl impurities caused general dark discoloration and pitting, with no deposit buildup. In the case of the oxygenated N_2O_4, no change in oxygen content occurred after one month storage whereas four month storage apparently resulted in O_2 depletion. An unexpectedly large negative oxygen value was obtained for the one month O_2/NOCl fluid, reported as a positive nitric oxide (NO) content. Apparently either an impurity was present or spurious reaction occurred to cause consumption of oxygen. It is not possible that the oxygenation apparatus leaked, however, it is conceivable that an error in weighing caused the anomalous value. No change in NOCl content was detectable in the O_2/NOCl fluid after one or four months.

Of interest is the very small degree of corrosion caused by the Cl_2 and NOCl contaminated N_2O_4, because it has been postulated that the chloride ion and/or molecular chlorine may be one of the principle species responsible for metal degradation in N_2O_4. The slight decrease in chlorine content is not considered significant in view of the fact that the specimens were not corroded significantly. Furthermore, they were extremely similar to the specimens exposed to uncontaminated N_2O_4. The larger values for NOCl content after storage are not particularly surprising as many instances of chloride buildup are reported in the literature.

347 Stainless Steel

The most severe attack was obtained in the O_2, H_2O, and O_2/NOCl contaminated N_2O_4 test fluids. Crystals formed on the specimen surface in the H_2O contaminated N_2O_4 were of a green color when viewed by reflected light, but were red when viewed by transmitted light. The crystals formed in the

O_2/NOCl contaminated N_2O_4 were red when viewed by eigher light mode, and in in addition, reacted vigorously (effervesced) when exposed to either atmospheric oxygen or water vapor. A significant water decrease and complete consumption of oxygen in the stainless steel tests were the most notable changes in contaminant additive. Once again an anomalous positive NO content results for the one month fluid contaminated with O_2/NOCl. The chlorine and NOCl contents changed moderately and insignificantly, respectively.

The general mode of corrosion for the stainless steel specimens was primarily minute pitting. Some surface roughening was also evident, however, since the objective of this task was to enhance, not suppress corrosion, none of the specimens were passivated prior to storage. The stainless steel specimens, however, did passivate to an extent, as can be noted from the thickness changes in the one and four month storage samples.

Ti-6Al-4V Alloy

The titanium alloy specimens were the least affected of any of the alloy systems by the corrodent fluids. The specimens appear somewhat darker than normal due to their high reflectivity. Some surface discoloration was evident on the specimens but they did not appear to be affected otherwise. No evidence of pitting or general attack was found in any of the specimens, and the only effect of the corrodent fluids noted was to slightly roughen the surface. In general, slight to moderate changes in contaminant level occurred with the exception of the four month O_2 and water concentrations which decreased markedly, though no corresponding increase in corrosion was found.

TABLE 1-8. Physical Appearance of One and Four Month Aluminum Specimens Prior To and After Removal of Propellant (N_2O_4)

Added Contaminant	Appearance of One Month Capsules		Appearance of Four Month Capsules	
	Before Propellant Removal	After Propellant Removal	Before Propellant Removal	After Propellant Removal
None	No noticeable corrosion.	No noticeable corrosion.	No noticeable corrosion.	Some oily substances on bottoms of tubes.
H_2O	Specimens covered with white salts.	Specimens covered with white salts.	White crystals on bottom of tubes. Specimens covered with white salts.	Specimens covered with white salts. Some crystals on walls and bottoms of tubes.
O_2	Slight spotted discoloration of specimens.	Slight spotted discoloration of specimens.	Slight discoloration.	Slight spotted discoloration of specimens. Yellow crystals at tops of the tubes. White powdery coating on the walls of the tubes.
NOCl	No noticeable corrosion.	No noticeable corrosion.	No noticeable corrosion.	No noticeable corrosion.
NOCl + O_2	Specimens slightly tarnished. One tube contained yellow gelatinous material.	Specimens appeared corroded. One tube had a yellow powdery coating at the top of the tube and a yellowish-brown gelatinous material. adhering to the walls.	Slight corrosion of specimens. One tube had yellow-green spots at the top of the liquid.	Specimens were slightly corroded. One tube had yellow particles at the top and a few on the bottom.
Cl_2	No noticeable corrosion.	No noticeable corrosion of specimens. One tube had a yellow ring at the N_2O_4 liquid-vapor interface.	No noticeable corrosion.	No noticeable corrosion.

TABLE 1-9. Physical Appearance of One and Four Month Stainless Steel Specimens Prior To and After Removal of Propellant (N_2O_4)

Added Contaminant	Appearance of One Month Capsules		Appearance of Four Month Capsules	
	Before Propellant Removal	After Propellant Removal	Before Propellant Removal	After Propellant Removal
None	No noticeable corrosion.	No noticeable corrosion.	No noticeable corrosion.	Some gelatinous material on the bottoms of the tubes. One tube had yellow coating on wall.
H_2O	Specimens were black with few black crystals on them. Greenish colored immiscible droplets on sides of tubes.	Specimens were black with few black crystals on them. Greenish colored immiscible droplets on sides of tubes.	Specimens were black with black crystals on them. Greenish colored immiscible droplets on sides of tubes.	Black salt crystals on specimens. Green oily substance on walls and bottom of tubes.
O_2	Specimens were black. Some yellow crystals on specimens and walls of the tubes. One tube had a few immiscible droplets.	Specimens were black and had some yellow crystals on them and on the tube walls. One tube had green immiscible droplets on it.	Specimens were black. Reddish-Brown crystals on walls of tubes above the liquid N_2O_4.	Specimens were black. Reddish-brown crystals on the walls of the tubes.
NOCl	No noticeable corrosion.	No noticeable corrosion.	Gelatinous material on the walls of the tubes. No noticeable corrosion of specimens.	Specimens are slightly discolored. Coating on the walls. No sign of gelatinous material.
NOCl + O_2	Specimens were black. Yellow crystals at the top of the liquid. Clear crystals on the bottoms of the tubes.	Specimens were black. Some yellow crystals and coating on the tops of the tubes.	Specimens were black. One tube had reddish-brown gelatinous material above and 1/2" below the liquid. Some gelatinous material on the tube wall.	Specimens were black and tube walls were coated. One tube had yellow crystals on the wall and the other tube had black spots.
Cl_2	Clear crystals on the tube walls. No noticeable corrosion of the specimens.	Slight discoloration of specimens.	No noticeable corrosion.	Slight discoloration of specimens. Reddish-brown crystals on bottoms of tubes.

TABLE 1-10. Physical Appearance of One and Four Month Titanium Specimens Prior To and After Removal of Propellant (N_2O_4)

Added Contaminant	Appearance of One Month Capsules		Appearance of Four Month Capsules	
	Before Propellant Removal	After Propellant Removal	Before Propellant Removal	After Propellant Removal
None	No noticeable corrosion.	No noticeable corrosion.	No noticeable corrosion.	A few crystals on the walls of the tubes.
H_2O	Specimens slightly spotted.	Specimens slightly spotted.	No noticeable corrosion.	Small amount of oily substance on bottoms of tubes. Clear crystals on walls of tubes.
O_2	No noticeable corrosion of the specimens. Tube walls covered with a yellowish-white material.	No noticeable corrosion of specimens. Tube walls coated with a yellowish-white substance.	No noticeable corrosion of specimens. One tube had reddish-yellow crystals on the wall above the liquid.	No noticeable corrosion. One tube had reddish-brown crystals above the liquid level.
NOCl	No noticeable corrosion.	No noticeable corrosion.	No noticeable corrosion.	No noticeable corrosion.
$NOCl + O_2$	A few clear crystals on the walls of the tubes.	No noticeable corrosion.	Clear colorless gelatinous material at the top of the liquid on the tube walls.	No noticeable corrosion. Yellowish-green immiscible droplets at the tops of the tubes and a few crystals on the bottoms.
Cl_2	No noticeable corrosion.	No noticeable corrosion.	No noticeable corrosion.	No noticeable corrosion.

TABLE 1-11. Rating Chart for Macroscopic and Microscopic Examination of Corrosion Behavior of Metals (After Champion)

NO.	Number of Pits		Size of Pits		Intensity of Corrosion			Factors Affecting Corrosion (% Influence)
	Chart A		Chart B		Chart C		Chart D	
	Standard Term	No. Per Sq. cm	Standard Term	Area (Sq. cm)	Standard Term	Depth of General Attack (cm)	Depth of Pitting or Cracking (cm)	
1	Very few	33	Minute	0.0006	Minute trace	0.0001	0.004	9
2	Few	100	Very small	0.003	Very small	0.0004	0.01	13
3	Small number	330	Small	0.016	Slight	0.0016	0.025	20
4	Moderate number	1,000	Moderate	0.08	Moderate	0.006	0.06	30
5	Considerable number	3,300	Considerable	0.4	Considerable	0.024	0.15	45
6	Numerous	10,000	Large	2.0	Severe	0.10	0.4	70
7	Very numerous	33,000	Very large	10.0	Very severe	0.40	1.0	100

TABLE 1-12 Results of One and Four Month Storage of 6061 T6 Aluminum Specimens With Neat and Contaminated N_2O_4 at 165°F.

FLUID CHARACTERIZATION				POST TEST METAL CHARACTERIZATION						
Added Impurities	Pretest Concentration % w/w	Storage Period, Months	Post Test Concentration % w/w	Weight Change mg	Thickness Change mil	Rating (b) A	B	C	D	Remarks
None	--	One	--	-0.3	-0.2	0	0	2	0	Little Discoloration.
		Four	--	-0.4	-0.1	1	1	0	0	Slight Discoloration.
Cl_2	0.101	One	0.060	+0.4	+0.4	0	0	(c)	0	Little or No Discoloration.
		Four	0.094	-0.2	-0.2	0	0	2	0	Slight Discoloration.
H_2O	0.91	One	0.82	-102.4	-0.6	3	2	3	2	Thick white coating on metal surface. General light discoloration after washing.
		Four	0.29	-111.1	-0.5	5	3	3	3	As Above.
O_2	0.04	One	0.04	-0.5	-0.3	4	2	2	3	General Dark Discoloration.
		Four	0	+1.4	-0.1	4	3	0	3	As Above.
NOCl	0.024	One	0.035	+0.2	-0.3	0	0	2	0	Little Discoloration.
		Four	0.030	-0.1	0.0	1	1	0	1	Slight Discoloration
NOCl + O_2	0.054	One	0.056 NOCl + 0.43 NO (a)	+1.0	-0.3	4	2	2	2	General Dark Discoloration.
	0.05	Four	0.054 NOCl + 0.07	+1.4	0.0	5	3	0	3	General Dark Discoloration.

(a) Oxygen apparently depleted and species formed which react with O_2.
(b) Rating of zero indicates negligible corrosion. See Table 1-11 for rating definitions.
(c) Corrosion rating not applicable because of deposit build-up.

TABLE 1-13. Results of One and Four Month Storage of 347 Stainless Steel Specimens With Neat and Contaminated N_2O_4 at 165°F.

FLUID CHARACTERIZATION				POST TEST METAL CHARACTERIZATION						
Added Impurities	Pretest Concentration % w/w	Storage Period, Months	Post Test Concentration % w/w	Weight Change mg	Thickness Change mil	Rating[b] A	B	C	D	Remarks
None	--	One	--	-2.3	-0.1	0	0	0	0	No Discoloration.
		Four	--	-2.2	+0.1	0	0	(c)	0	No Discoloration.
Cl_2	0.101	One	0.075	-1.6	-0.1	0	0	0	0	No Discoloration.
		Four	0.068	-2.5	+0.2	0	0	(c)	0	Slight Discoloration.
H_2O	0.91	One	1.1	5.6	-0.4	1	1	3	1	Small crystals on metal surface. General dark discoloration.
		Four	0.48	-54.1	-0.1	4	1	0	2	As Above.
O_2	0.04	One	0.07 NO[a]	-24.0	-0.2	4	2	2	3	Small crystals on metal surface. General dark discoloration.
		Four	0.01 NO[a]	-28.8	0.0	4	2	0	3	As Above.
NOCl	0.024	One	0.020	-0.8	-0.2	0	0	2	0	No Discoloration.
		Four	0.020	-1.5	+0.1	0	0	(c)	0	No Discoloration.
NOCl + O_2	0.054 + 0.05	One	0.072 NOCl + 0.33 NO[a]	-37.2	-0.2	2	2	2	2	Small crystals on metal surface. General dark discoloration.
		Four	0.053 NOCl + 0.03	-33.5	+0.1	4	2	(c)	2	As Above.

(a) Oxygen apparently depleted and species formed which react with O_2.
(b) Rating of zero indicates negligible corrosion. See table 1-11 for rating definitions.
(c) Corrosion rating not applicable because of deposit build-up.

TABLE 1-14. Results of One and Four Month Storage of Ti-6Al-4V Alloy Specimens With Neat and Contaminated N_2O_4 at 165°F.

FLUID CHARACTERIZATION				POST TEST METAL CHARACTERIZATION							
Added Impurities	Pretest Concentration % w/w	Storage Period, Months	Post Test Concentration % w/w	Weight Change mg	Thickness Change mil	Rating[b] A	B	C	D	Remarks
None	--	One	--	-0.2	-0.1	0	0	0	0	Minute Discoloration.
		Four	--	-0.1	+0.2	0	0	(c)	0	Slight Discoloration.
Cl_2	0.101	One	0.084	-0.3	+0.4	0	0	(c)	0	Minute Discoloration.
		Four	0.058	-0.0	+0.2	0	0	6	0	Slight Discoloration.
H_2O	0.91	One	1.37	0.0	0.0	0	0	0	0	General Medium Discoloration.
		Four	0.52	+0.2	+0.2	0	0	(c)	0	As Above.
O_2	0.04	One	0.12	-3.6	-0.1	0	0	0	0	No Discoloration.
		Four	0.04 NO[a]	-0.6	+0.2	0	0	(c)	0	Slight Discoloration.
NOCl	0.024	One	0.018	-0.2	0.0	0	0	0	0	No Discoloration.
		Four	0.017	-0.1	+0.1	0	0	(c)	0	Slight Discoloration.
NOCl + O_2	0.054	One	0.060 NOCl 0.09 +	-6.0	-0.1	0	0	0	0	Minute Discoloration.
	0.05	Four	0.043 NOCl 0.09 +	-4.1	0.0	0	0	0	0	Slight Discoloration.

(a) Oxygen apparently depleted - oxygen reactive species present.
(b) Rating of zero indicates negligible corrosion. See table 1-11 for rating definitions.
(c) Corrosion rating not applicable because of deposit build-up.

FUELS

DIBORANE (B_2H_6)

Diborane is used as a high energy fuel. It is extremely toxic. Diborane is insensitive to mechanical shock and exhibits satisfactory (77°F) thermal stability in an inert atmosphere. It exhibits hypergolicity with the high energy oxidizers and behaves as a strong reducing agent in oxidation reduction reactions.

Diborane has a distinctive odor described as rotten eggs, sickly sweet and musty or foul. The recommended threshold limit is 0.1 ppm for an 8 hour exposure. Toxic concentrations are reached before any odor is detected. The ability to detect the odor decreases with exposure, therefore, special detectors must be used. Any substance which will function as a potential oxidizer will react with diborane including such materials as water, air, some metal oxides and reducible organic compounds. Diborane decomposes slowly at room temperature to hydrogen and high-molecular weight boran hydrides. Diborane is completely hydrolized by water:

$$6H_2O + B_2H_6 \longrightarrow 2B(OH)_3 + 6H_2$$

The compatibility of diborane with other materials is similar to those listed under pentaborane except that diborane is somewhat more reactive than pentaborane at normal storage temperatures. In comparing chemical compatibility of pentaborane with diborane consideration should be given to problems associated with the lower temperature of the gaseous state of diborane.

Table 1-15 lists the materials considered to be most recommended for diborane. In all cases, these materials are suitable only if strict control of surface contamination and careful attention to minimize thermal

fluctuations above -20°C are maintained. In regard to cleanliness, selection and complete removal of cleaning solvents requires special consideration since diborane may react explosively with certain hologenated solvents, e.g., carbon tetrachloride.

PHYSICAL PROPERTIES

Molecular Weight	27.69
Freezing Temperature °F	-265
Normal Boiling Point °F	-134
Critical Temperature °F	62
Critical Pressure psia	581
Heat of Vaporization Btu/lb_m	414
Density, gm/cc	0.47(-250)

TABLE 1-15. DIBORANE

COMPATIBILITY OF MATERIALS FOR LONG TERM APPLICATION

COMPATIBLE MATERIALS	INCOMPATIBLE MATERIALS
Metals	Non-Metals
Stainless Steel 18-8 Series	Most Natural and Synthetic Elastomers
Low Carbon Steels	Silicone Grease [a]
Nickel	Fluorolube FS [a]
Monel	
Brass	
Non-Metals	
50-50 Polyethylene Polyisobutalene	
Kel-F	
Glyptal	
Vaseline-Paraffin-Graphite	
Asbestos-Graphite-Copper Packings	

a These materials absorb small quantities of diborane and thus are suitable for limited service only.

HYBALINE A-5

Hybaline A-5 is a pyrophoric, high energy fuel blend, of low volatility and reacts violently with water. Its composition is classified.

Cursory tests have been performed on some materials, although no definitive evaluation has as yet been conducted. Two separate investigations have been performed on the compatibility and corrosion rates of structural materials in Hybaline A-5 liquid and vapor at 50°C (122°F). Some discrepancy is noted on the compatibility of copper and brass toward the decomposition of Hybaline A-5, thus, caution is recommended until extensive investigation resolves these differences. The primary corrosion agents in the mixture are chlorides, utilized in the synthesis, which are not completely removed from the product.

The results of the two investigations are listed in Table 1-16. Materials listed as compatible have low (0.1 MPY avg.) corrosion rates and/or do not catalyze the decomposition of Hybaline A-5.

Discussion of Problem Areas -

Hybaline A-5

Metals, Ceramics, Organic Polymers, Wet and Dry Lubes (2)* - There is not sufficient data available on Hybaline A-5 to enable a reliable assessment of materials compatibility, but it would appear that no serious problems exist with these materials.

*Parenthetical enclosures refer to Propellant Rating Chart, Page 1-11.

TABLE 1-16. HYBALINE A-5

COMPATIBILITY OF MATERIALS AT 122°F

COMPATIBLE METALS	NON-COMPATIBLE METALS
ALUMINUM	Copper[a]
1100[a]	Brass[a]
2104-T6	
2024-T3	
6061-T6	
7075-T6	
7075-T73	
356-T6	
Titanium Alloy A-110 AT[a]	
STAINLESS STEELS	
17-7 PH[a]	
17-4 PH	
302	
304L[a]	
316	
321	
347	
410	

NON-METALS	NON-METALS
Mylar[a]	Neoprene
Teflon (TFE and FEP)[a]	Viton-A
Kynar[a]	Tygon
Polyethylene[a]	Ke-F 90
Buna-N[a]	Fluorolube 362
Halocarbon Grease[a]	Dow Corning Valve
Dow Corning Hi-Vac Oil[a]	Seal Aerochlor 1254

a - exposure for 2 months. Other data is for a static, twenty-one day test.

LIQUID PETROLEUM GASES (LPG) PROPELLANTS

The LPG propellants are colorless, flammable hydrocarbons, which are normally gaseous at room temperature and atmospheric pressure. The primary pure materials of interest are methane, propane, and butene. A pentane blend has also been proposed for use. The LPG propellants are not considered toxic gases. Methane acts physiologically as a simple asphyxiant. Butene and propane, in higher concentrations, also have an anesthetic action. Self-contained breathing apparatus, therefore, should be used if there is a suspected high concentration of these gases present, as in the case of a spill, etc. The LPG propellants should be stored away from any oxidizer and from possible sources of ignitions. All metallic equipment required for storage and handling should be grounded in order to prevent an accumulation of static charge.

Since the LPG propellants are non-corrosive, any common or commercially available metal may be used in the LPG is in the gaseous state. Metals having acceptable low temperature physical properties must be utilized in storing liquid methane, however, since it boils at -259°F (1 atm).

Inasmuch as the propellants are hydrocarbons, they exert a solvent action on many greases, plastics and rubbers. Thus, consideration must be given to the types of organic materials which may come in contract with the propellants. Teflon, nylon, and the alkylene polysulfides are all resistant to attack, with the neoprene and butadiene-acrylonitrile rubbers being slightly less resistant.

PHYSICAL PROPERTIES

	Methane	Propane	1-Butene
Molecular weight	16.04	44.10	56.10
Freezing point °F at 1 atm	-296	-306	-303
Normal boiling point °F at 1 atm	-259	-44	20.7
Critical pressure, psia	693	617	583
Latent heat of vaporization, cal/g	121.9	101.8	93.4

Discussion of Problem Areas -
Liquified Petroleum Gases (LPG) Propellants

Radiation Tolerance (2)* - Since butene is an unsaturated hydrocarbon, reactions such as polymerization or molecular rearrangement can occur. Polymerization by free radical extension is normally carried out using catalysts, but can be induced by ionizing radiation. If the polymerization initiation is widespread throughout the storage tank, a violent and uncontrollable reaction may take place. Slow polymerization may result in the formation of sludge or varnish, leading to system malfunction.

Wet and Dry Lubes (2-3) - Because of the solvent properties of the propellants, there tend to be undesirable "wash-out" effects on lubricants. These problems can be minimized by the use of glands and seals. Experience in the petroleum industry with such lubricants as Plastilube #1 (Lubrication Company of America), John Crane Insoluble Gasoline Lubricant (Crane Packing Company), and Dow Corning Valve Seal (Dow Corning), indicated that these materials may be satisfactory for use.

Effects of Leakage (2) - Because of the extensive flammability of the propellants, the main hazard lies in the accumulation of vapors in confined areas, where the possibility of accidental ignition can occur. However, inasmuch as the gases are non-toxic, possess low flammability limits and since reliable vapor detectors are available, proper ventilation and elimination of sources of ignition reduce the danger of fire or explosion.

*Parenthetical enclosures refer to the Propellant Rating Chart, Page 1-11.

SPACE STORABLE PROPELLANTS (Continued)
OXIDIZERS

CHLORINE TRIFLUORIDE (CTF) (ClF_3)

Chloride trifluoride, like fluorine, is among the most active chemicals known. Being a very strong oxidizing agent, it reacts vigorously with most oxidizable substances at room temperature and with most common metals at elevated temperatures. Under ordinary conditions, chlorine trifluoride reacts violently with water or ice. It is, however, insensitive to mechanical shock, nonflammable in dry air, and shows good thermal stability at ambient temperatures. Although some surface staining has occurred in tests employing impact, there has been no evidence of ignition utilizing aluminum, copper, magnesium or titanium in either gaseous or liquid CTF. Since CTF is probably the most corrosive and toxic of the interhalogens, the materials and precautions given for it are sufficient for use with the other halogen fluorides.

The corrosion resistance of all materials of construction used with chlorine trifluoride depends on the formation of a passive metal fluoride film which protects the metal from further attack. It is important that this film exhibit a tenacious bond with the parent material and not be easily removed or soluble in the CTF. Successive wearing operations can destroy the film and result in a "pseudo-corrosion rate" which is due to the inability of the film to withstand the operation and not due to a basic incompatibility of the material. The ability of some metals such as Monel, copper, nickel, stainless steel, etc., to form this tenacious, passive, metal-fluoride film makes them resistant to attack by chlorine trifluoride. Among the metals mentioned, Monel and nickel are preferred because of their resistance to hydrogen fluoride and hydrogen chloride, which are formed by the reaction of chlorine trifluoride with water. Aluminum alloys, 18-8 stainless steels and K Monel have been used for bellow materials. Gaskets have been made from sterling silver and lead-indium alloys, copper braid backed in Teflon, and calcium fluoride filled Teflon. Tin, indium carbon and boron carbide have been used for rotating seals.

Table 1-17 lists those materials which are considered to be compatible with chlorine trifluoride under most conditions for long-term application. However, materials that are listed in the table must be thoroughly cleaned and passivated (in the case of metal) to insure a contamination-free surface. All chlorine trifluoride systems must also be dry and leak-proof.

PHYSICAL PROPERTIES

Specific Gravity	1.83 (60°F)
Molecular Weight	92.46
Freezing Temperature °F	-105
Normal Boiling Point °F	53
Critical Temperature °F	345
Critical Pressure psia	838
Heat of Vaporization Btu/lb_m	128

Discussion of Problem Areas -
Chlorine Trifluoride (ClF_3)

Organic Polymers (1-2)* - most organic polymers undergo spontaneious ignition and/or absorption of ClF_3 to form detonable mixtures, hence use of components incorporating plastic mat4erials is not recommended. Teflon and Kel-F have been found acceptable under static propellant (nonflow) conditions; however, they may ignite when heated.

Wet and Dry Lubes (1) - No completely satisfactory lubricant is known. Most lubricants ignite spontaneously and/or form detonable mixtures with chlorine trifluoride. However, see remarks under fluorine.

*Parenthetical enclosures refer to Propellant Rating Chart, Page 1-11.

Effects of Leakage (1) - Leakage cannot be tolerated in valves used for chlorine trifluoride. Although ClF_3 is nonflammable in air and exhibits excellent thermal stability at ambient temperatures, it does represent an extremely hazardous propellant due to its toxicity and extreme reactivity with the vast majority of organic and inorganic compounds. At elevated temperatures it will react vigorously with most common metals; the propellant readily ignites organic materials such as solvents and lubricants. Space leakage is discussed under hydrazine.

Soft Seats (1-2) - Soft seats made of plastic materials generally are unsuitable for service with chlorine trifluoride. Some success has been found using Teflon impregnated with 40% calcium fluoride.

Hard Seats (2) - A very limited number of soft metals (principally aluminum 1100 and copper) have been found satisfactory for valve seat use. The seats should be thoroughly cleaned and propellant passivated prior to installation.

TABLE 1-17. CHLORINE TRIFLUORIDE (CIF_3)

MATERIAL	TEMP °F
ALUMINUM ALLOYS	
1060	85
1100	85
2014	85
2024	85
3003	85
5052	85
6061 (Welded)	85
6063	
6066	
356	
Tens 50	
STAINLESS STEEL	
301	
302	
303	85
304	85
316	85
321	
347	85
403	85
PH 15-7 Mo	85
410	85

MATERIAL	TEMP °F
OTHER METALS	
A-Nickel	85
Copper	85
Incoloy	85
Inconel	85
Indium	
Lead Indium Alloy	
Tin Indium Alloy	
Magnesium AZ-31B	85
Magnesium HM-21A	85
Magnesium HK-31A	85
Monel	85
K. Monel	
Nitralloy	
Silver Solder	
Sterling Silver	
Tin	
NON-METALS	
Boron Carbide	
Carbon	
Kel-F (Under Static Cond. Only)	
Teflon (Under Static Cond. Only)	
Teflon-40% CaF_2	

Note 1: Materials listed above are rated compatible based on a corrosion rate of less than 1 mil per year and the material does not cause decomposition, and is free from impact sensitivity. Non-metals are rated for satisfactory service for general use.

CHLORINE PENTAFLUORIDE

Chlorine Pentafluoride is among one of the most energetic oxidizers in use as a rocket propellant.

Immersion of TFE Teflon and Kel-F in liquid Chlorine Pentafluoride up to 86°F resulted in moderate weight gains, particularly for Kel-F. Complete and rapid reaction of columbium and molybdenum and degradation of blocks of carbon and graphite to powders resulted from immersion in this propellant. There was no change in titanium from immersion in Chlorine Pentafluoride however. Ignition could not be initiated by impassing aluminum 2014-T6, magnesium AZ 31B, nickel 200, or 347 stainless at 65 ft-lbs in the liquid at 86°F. Teflon TFE violently reacted when impacted under similar circumstances with 410 stainless. Table 1-18 lists those materials which showed minimal corrosion rates at 86°F or 150°F.

Discussion of Problem Areas -
Chlorine Pentafluoride

Organic Polymers (1-2)* - Most organic polymers undergo spontaneous ignition and/or absorption to form detonable mixtures, hence use of components incorporating plastic materials is recommended. Teflon TFE and FEP have been found satisfactory under static propellant conditions; however, they may ignite when heated or impacted.

Wet and Dry Lubes (1) - No completely satisfactory lubricant is known. Most lubricants ignite spontaneously and/or form detonable mixtures.

Effects of Leakage (1) - Leakage through valves presents a serious hazard, due to its toxicity and reactivity with most known materials. In addition, the effect of leakage is usually to increase the size of the leakage passage and thus present an increasing exposure threat to its surrounding environment. Space leakage is discussed under Hydrazine.

*Parenthetical enclosures refer to Propellant Rating Chart, Page 1-11.

Soft Seats (1-2) - Soft seats made of plastic are unsuitable for service. CaF_2 - filled Teflon might be applicable under special conditions.

Hard Seats (2) - No data is available, but probably valve seats found suitable for use in the more energetic oxidizers would prove satisfactory.

TABLE 1-18. CHLORINE PENTAFLUORIDE

MATERIAL	CORROSION RATE MPY (21 day storage)	
	86°F	150°F
Aluminum 2014-T6	0.03	0.00
Aluminum 6061-T6	0.13	0.66
Yellow Brass, 1/2 Hard	0.07	0.17
Copper ETP, Soft Temper	0.06	0.07
Magnesium AZ 31B-0	0.00	0.00
Monel 400, Annealed	0.00	0.01
Nickel 200, Annealed	0.00	0.00
347 SS, Hot-rolled	0.00	0.67
410 SS, 180-200 ksi T.S.		

*Parenthetical enclosures refer to Propellant Rating Chart, Page 1-11.

OXYGEN DIFLUORIDE (OF_2)

Oxygen difluoride is a colorless gas at room temperature and atmospheric pressure, condensing to a yellow liquid at -229°F. It has a foul odor. The limit of detectability appears to be in the range of 0.1 ppm; 0.5 ppm in air is easily detected. Based on present knowledge, oxygen difluoride must be regarded as a highly toxic gas, possessing the same lethal characteristics as phosgene.

Oxygen difluoride is a powerful oxidizing agent similar to fluorine and the halogen fluorides, but is generally considered to be much less reactive than fluorine. It is capable of reacting with a majority of inorganic and organic compounds provided sufficient activation energy is available.

When reaction with OF_2 occurs, high heats of reaction are common, many sufficiently energetic to cause ignition. Reports on hypergolicity of fuels such as hydrazine, ammonia and monomethylhydrazine give varying conclusions; hence, the materials should be treated as potentially hypergolic at all times. Oxygen difluoride and diborane are unquestionably hypergolic. Oxygen difluoride is a relatively stable compound in that it does not detonate by sparking and was found to be insensitive to shock at -320°F. It does, however, begin to decompose thermally at approximately 480°F.

The data for materials compatibility are limited, but they do show that no major problems are to be expected with the majority of metals. A few metals including Titanium 110 AT, tantalum, magnesium and lead, exhibit moderate-to-violent reactions when subjected to shock loading in the presence of OF_2. In like manner, Teflon, Kel-F and graphite indicate shock sensitivity. Parts made of these materials are not suitable for OF_2 applications if shock or impact loading is a requirement. On the other hand, there exists some service experience with valves containing fluorinated polymers such as Teflon, Alcar and Halon in contact with the liquid phase.* These data are insufficient, but results are reported to be encouraging. Oxygen difluoride can be handled readily in most common metals and glass, with the choice dependent

* Although most data indicate that these materials are recommended for gas phase service only.

upon the service requirement. Metals such as stainless steel, copper, aluminum, Monel, and nickel may be used for gas and liquid service from cryogenic temperatures to approximately 400°F.

Table 1-19 lists the materials considered to be compatible with oxygen difluoride. Tests were conducted with liquid OF_2 at -109°F.

PHYSICAL PROPERTIES

Specific Gravity	1.496 (-288.8°F)
Molecular Weight	54.00
Freezing Temperature °F	-370.8
Normal Boiling Point °F	-288.6
Critical Temperature °F	-72.8
Critical Pressure psia	719

Discussion of Problem Areas -
Oxygen Difluoride (OF_2)

Ceramics (2)* - Oxygen difluoride exhibits a strong oxidizing power similar to that of fluorine, and thus reacts with the vast majority of inorganic and organic materials. Extreme care should be taken to select materials compatible with the propellant under the temperature extremes of its environment.

Organic Polymers (2) - Polymers such as Teflon (TFE and FEP), Kel-F-81, the fluorosilicones, and the vinyl silicone elastomers have been utilized for limited service at moderate temperatures.

Wet and Dry Lubes (1) - There is no known lubricant for use in contact with liquid or gaseous oxygen difluoride. Because of the high reactivity of OF_2 with organic materials, conventional lubricants should definitely be avoided. Even the most likely candidates, the normally unreactive perfluorinated hydrocarbon lubricants, are degraded in the presence of liquid or gaseous OF_2. It is therefore recommended that all valves be designed so as to eliminate the use of a lubricant in intimate contact with this oxidizer.

*Parenthetical enclosures refer to Propellant Rating Chart, Page 1-11.

Soft Seats (1)* - Soft seat materials are often used at cryogenic temperatures, however this use is normally limited to polymers rather than elastomers. Extreme care must be used with polymers in OF_2 service due to possible reaction with the propellant. The use of polymers should be limited to static seals not exposed to the flow stream. All metal valves with metal to metal seats are preferred.

Effects of Leakage (1) - Oxygen difluoride displays properties similar to those of liquid fluorine, but is generally considered to be less reactive and easier to handle. It is a relatively stable material in that it does not detonate by sparking, but it does begin to decompose thermally at elevated temperatures (about 480°F). Tests of reactivity to fuels such as hydrazine, ammonia, and monomethylhydrazine have given varied results as to its hypergolic nature. However, it should be assumed that the oxidizer is hypergolic with all fuels because of its very strong oxidizing power. The data on toxicity are quite limited, but OF_2 must be regarded as a highly toxic material, similar to phosgene. Space leakage problems are similar to those discussed for Hydrazine.

*Parenthetical enclosures refer to Propellant Rating Chart, Page 1-11.

TABLE 1-19. OXYGEN DIFLUORIDE

COMPATIBILITY OF MATERIALS AT -109°F[(a)]

MATERIAL	MATERIAL
METALS	OTHER METALS
ALUMINUM	PH 15-7 Mo
1100-0	AM-350
2014-T6	Nickel 200
2219-T6	Inconel X
6061-T6	Rene 41
7079-T6	Cufenloy 40
	Cufenloy with electroless Ni plate
STAINLESS	Copper
301	Brass 7030
316	Columbium
347	
410	

(a) Metals listed above are rated compatible based on a corrosion rate of less than 1 mil per year, and the material does not cause decomposition and is free of impact sensitivity.

COMPATIBILITY OF MATERIALS FOR SHORT TERM USE

MATERIAL	REMARKS
ALUMINUM ALLOYS	
2024-T3	*
2024-T3 (Alclad)	*
STAINLESS STEEL	
301	*
304	
Maraging AM 355	*(No change for gas at ambient temperature)
Maraging AM 367	*

*Fluoride coatings formed, but weight gain was considered insignificant.

OXYGEN DIFLUORIDE

COMPATIBILITY OF MATERIALS FOR SHORT TERM USE (Continued)

MATERIAL	REMARKS
OTHER METALS	
Beryllium Copper (2%)	*
Inconel X750	
Magnesium AZ 31B, H24	*
Monel 400	*
Monel K500	*
Titanium Alloy 5Al-2.5 Sn	
NON-METALS	
Glass	Above 390°F, glass is attacked by OF_2

*Fluoride coatings formed, but weight gain was considered insignificant.

INCOMPATIBLE MATERIALS*

INCOMPATIBLE METALS	INCOMPATIBLE NON-METALS
Titanium A110-AT	Graphite
Titanium 6Al-4V	Teflon TFE
Lead	Teflon FEP
	Kel-F 5909
Tantalum	Kel-F Resin
	Oxylube 701
Magnesium HM21A-T8	

*Incompatibility with OF_2 is based on impact sensitivity.

PERCHLORYL FLUORIDE (PF) ($FClO_3$ or ClO_3F)

Perchloryl fluoride is a colorless gas at ambient conditions with a characteristic sweetish odor. Under pressure or low temperature it is storable in liquid form. The toxic action of perchloryl fluoride is derived from its pronounced oxidizing properties and results in respiratory irritation, oxidation of hemoglobin and absorption of fluoride into the body. The toxicity threshold limit for perchloryl fluoride in air is 3 ppm.

Perchloryl fluoride is thermally stable up to 849°F in absence of air. It is nonflammable but, being a strong oxidizing agent, readily supports combustion of many organic materials. Although not shock sensitive itself, in combination with porous organic or inorganic materials it can produce a potentially shock-sensitive mixture. Combinations of perchloryl fluoride and most rocket fuels constitute explosion hazards.

Reactions of perchloryl fluoride with water is very slow up to about 575°F. However, in the presence of water, perchloryl fluoride becomes more corrosive. The corrosion resistance of metals of construction therefore depends largely on the quantity of moisture present, hence selection must be governed by the mositure content. Under mositure conditions, types 304, 310, and 314 stainless steels have shown good resistance at room temperature.

Teflon and Kel-F are very resistant to attack by perchloryl fluoride. Other plastics which are suitable are unmodified phenolic resins and epoxy resins. Under mild conditions of heat shock, Teflon, Kel-F and Kaynar can be used, but may undergo structural changes when moderate amounts of perchloryl fluoride are absorbed. These plastics should not be used under dynamic flow conditions such as would result in their use with valves, since the resultant swelling of seal materials so constituted presents problems of physical interference.

Table 1-20 lists materials suitable for use with perchloryl fluoride.

PHYSICAL PROPERTIES

Specific Gravity	1.69 (-52.2°F)
Molecular Weight	102.457
Freezing Temperature °F	-231
Normal Boiling Point °F	-52.2
Critical Temperature °F	202
Critical Pressure psia	779
Heat of Vaporization Btu/lb_m	84.0

Discussion of Problem Areas -
Perchloryl Fluoride ($FClO_3$)

Metals (2-3)* - Although anhydrous perchloryl fluoride (less reactive and corrosive than other halogen-containing oxidants) at ordinary temperatures is not reactive to most common metals, selection of a metal for use with this propellant should be governed by the moisture content. In the presence of water, perchloryl fluoride is corrosive to most metals. The readily oxidized metals will burn in perchloryl fluoride under severe conditions; therefore, extreme care must be taken in selecting metals with thorough knowledge of propellant purity, compatibility, and potential environmental extremes.

Organic Polymers (2) - Many organic materials do not react with perchloryl fluoride at ambient temperature, but if ignited, will burn violently; some are hypergolic. Hence, materials compatibility is extremely important in the selection of a polymeric material. Teflon and Kel-F appear to be resistant to attack, but tend to absorb the fuel. Some phenolic and epoxy resins have found limited use.

*Parenthetical enclosures refer to Propellant Rating Chart, Page

Wet and Dry Lubes (1-2) - Fluorocarbons are the only suitable lubricants. Perchloryl fluoride must not be brought into contact with any other conventional valve grease or oil.

Effects of Leakage (1-2) - Perchloryl fluoride leakage represents an acute toxic hazard. Because of its strong oxidizing effect, it readily supports combustion with oxidizable materials such as organic compounds; it is hypergolic with some fuels such as hydrazine, and in combination with most other fuels may detonate. Space effects of leakage are discussed under hydrazine.

Soft Seats (2) - Teflon and Kel-F seats are recommended for limited use; however, consideration must be given to their ability to absorb perchloryl fluoride.

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*Parenthetical enclosures refer to Propellant Rating Chart, Page 1-11.

TABLE 1-20. PERCHLORYL CHLORIDE

COMPATIBILITY OF MATERIALS FOR LONG TERM APPLICATION (NOTE 1)

MATERIALS	TEST TEMP °F
ALUMINUM ALLOYS	
1060	85
1100	85
2014	85
2024	85
3003	85
5052	85
6061	85
7079	85
STAINLESS STEELS	
304	85*
316	85*
347	85
403	85
410	85
Carpenter No. 20-Cb	85*
PH 15-7 Mo (Cond. RH 950)	85
PH 15-7 Mo (Cond. TH 1050)	85
AM 350 (Welded)	85
COPPER ALLOYS	
Aluminum Bronze, 8% Ampco 8	85
Beryllium Copper, 2%	85
Nickel Silver, 18% Alloy A	85
Phosphor Bronze, 5% Grade A	85
Rule Brass	85
Yellow Brass	85
Copper, ETP	85
Copper, DHP	85
MAGNESIUM ALLOYS	
AZ-31B	85
HK-31A	85
HM-21A	85
NICKEL ALLOYS	
"A" Nickel	85
Nickel 200	85
Inconel	85*
Incoloy	85*
Monel	85
Ni-o-Nel	85*
LOW CARBON STEELS	
1010	85
1010 (Coated w/Fosbond 40)	85
1010 (Coated w/Fosbond 27)	85
MISCELLANEOUS METALS	
Gold	85*
Platinum	85*
Silver	85*
PLASTICS AND ELASTOMERS	
Teflon	
Kel-F	
Polyethylene	

*Moisture content to 1%.

NOTE 1: Metals listed above are rated compatible based on a corrosion rate of less than 1 mil per year and the material does not cause decomposition, and is free from impact sensitivity Non-metals are rated for satisfactory service for general use.

NITROGEN-FLUORINE COMPOUNDS

This family of chemical compounds includes three oxidizers which have limited usage as storable propellants. Included are nitrogen trifluoride (NF_3), tetrafluorohydrazine (N_2F_4) and nitryl fluoride (NO_2F). Usage is limited because these oxidizers present most of the normal problems associated with corrosive cryogenic propellants but do not yield as high a specific impulse as other oxidizers such as liquid fluorine and oxygen difluoride. The main interest in these oxidizers stems from the fact that they have become building blocks toward the production of other N-F compounds that have higher boiling points, hence, are more easily storable. Inasmuch as compatibility data is limited, separate compatibility tables are not included, but discussed under each propellant.

Nitrogen Trifluoride (NF_3)

Nitrogen trifluoride is a colorless gas at room temperature and atmospheric pressure which condenses to a liquid at -200°F. It is relatively easy to prepare, thus potentially inexpensive. As a gas it is fairly stable and non-corrosive. As a liquid it is similar to liquid fluorine in that it is highly reactive with certain fuels. Materials compatibility data is very limited. Glass, stainless steel, nickel, copper and monel are suitable for use with this oxidizer.

Nitryl Fluoride (NO_2F)

Nitryl fluoride is a gas at room temperature and atmospheric pressure which condenses to a liquid at -82°F. It is highly reactive, even attacking glass. Reaction with metals and non-metals differs from the above two oxidizers because of the oxygen present. Most metals, including aluminum, steel, and titanium react to form both an oxide and a fluoride. Most non-metals react to form nitronium salts. Beryllium, magnesium, and gold do not react with nitryl fluoride below 300°F.

Tetrafluorohydrazine (N_2F_4)

This oxidizer is similar to nitrogen trifluoride but is slightly heavier. At room temperature and atmospheric pressure, it is a gas, and condenses to a liquid at -100°F. Compatibility data is scarce, but will be similar to that supplied for NF_3.

HARD CRYOGENICS

LIQUID FLUORINE (LF_2)

Fluorine is the most powerful chemical oxidizing agent known. It reacts with practically all organic and inorganic substances, with a few exceptions being the inert gases, some metal fluorides and a few uncontaminated fluorinated organic compounds. It exhibits excellent thermal stability and resistance to catalytic breakdown, thereby presenting little or no problem in these areas. Compatibility ratings are, therefore, based primarily on the reaction of the fluorine with the various materials used.

Although fluorine is the most chemically active of all elements, many of the common metals can be considered for use in liquid fluorine systems.

Fluorine is a liquid at atmospheric pressure only in the short temperature range of -306°F to -363°F, therefore requiring insulation of all valves. At these low temperatures chemical reactions in general tend to take place rather slowly, thus corrosive attack by the liquid fluorine is generated at a slower rate. Another factor responsible for low rate of attack by liquid fluorine on the common metals is that protective films of fluoride compounds tend to form on metal surfaces and act as a barrier to further reaction. These films, however, must be tenaciously held by the parent material in order to retain their effectiveness.

The effectiveness of the protective film formed on the metals by the liquid fluorine also is based on the solubility of the various metal fluorides that form in the film in fluorine. It is believed that, as a protective film builds up and the rate of reaction slows down, an equilibrium between reactive rate and solubility of the film will be reached and a relatively steady corrosion rate will result. Lack of solubility data for fluorine compounds and corrosion rates for long periods of exposure can only be supplemented by actual service data and extrpolation of existing data. Service data indicate that the fluorides of nickel,

copper, chromium and iron are relatively insoluble in liquid fluorine. Also, metals such as Monel, nickel and stainless steels exhibit satisfactory performance in liquid fluorine and indications are that much lower rates of corrosion can be expected for long-term exposure where equilibrium rates are reached, than for short-term laboratory exposure. Some experiments, however, have shown that there is no increased corrosion of specimens immersed in liquid fluorine and wirebrushed to remove any films. This suggests that either not all the passivating effect is from formation of a metal fluoride film, or that the thickness of the film necessary for protection can be extremely thin.

Several lightweight metals such as the alloys of aluminum, titanium and magnesium are also known to produce protective films in liquid fluorine. Of these, titanium probably exhibits the lowest rate of corrosion; however, tests have shown it to be impact sensitive in fluorine.

Other factors to consider in selecting materials for use in a liquid fluorine system are: 1) flow rates, 2) water contamination in the system, and 3) mechanical properties of the material at the low temperatures experienced with liquid fluorine. The rate of flow of the liquid fluorine in a valve and through an orifice is considered to be an important factor in maintaining the protective film on the materials being attacked. Fluoride coatings on some metals that are less resistant to fluorine, such as low-alloy steels, are sometimes very brittle or porous and powdery. High flow rates tend to remove these coatings and thus increase corrosive action. In restricted flow applications "flaking" of the coating may result in contamination of the propellant, thus creating leakage problems at the valve seat.

Teflon has withstood exposure to liquid fluorine in a static condition. However, Teflon tends to react with fluorine to break down the polymers and form unsaturated low molecular weight fluorocarbons which do not adhere to the surface. Any flow of the propellant or movement of material over the surface of Teflon will remove these fluorocarbons, thus leaving them valueless as a protective film. Impurities introduced in the

manufacturing process appear to be responsible for accelerated decomposition of Teflon in liquid fluorine service.

Fluorine will react with any water present in the system to form hydrofluoric acid. This acid tends to attack some materials that are normally resistant to uncontaminated fluorine. Of all the metals showing resistivity to fluorine attack, Monel is generally preferred for use because of its inherent resistivity to the hydrofluoric acid.

In selecting materials for use in fluorine systems, consideration should also be given to the effects of low temperature environment on the mechanical properties of the materials. Some metals, such as the martensitic stainless steels, become brittle at these low temperatures.

Table 1-21 lists those materials which are considered to be compatible for service with liquid fluorine. However, as previously stated, insufficient information on prolonged usage of these materials in liquid fluorine restricts any rating for long-term application. Also, before using any material with fluorine, extreme care should be exercised in cleaning the material thoroughly to remove all possible contamination that may be present. Pre-treatment or conditioning treatment is also recommended. After thoroughly cleaning the material, a conditioning treatment exposes the material at room temperature to pure fluorine gas or a mixture of fluorine diluted with an inert gas. This, it is believed, initiates the formation of a relatively inert fluoride film. With the use of a diluted gas, the reaction that may take place with any traces of contamination remaining after cleaning would be less violent in nature. This treatment will then permit the material to withstand attack by full strength fluorine with much less reaction.

PHYSICAL PROPERTIES

Specific Gravity	1.69 (-52.2°F)
Molecular Weight	102.457
Freezing Temperature °F	-231
Normal Boiling Point °F	-52.2
Critical Temperature °F	202
Critical Pressure psia	779
Heat of Vaporization Btu/lb_m	84.0

Discussion of Problem Areas -

Liquid Fluorine (F_2)

Ceramics (2-3)* - There are few ceramic materials which are completely satisfactory for use with liquid fluorine, although some have found limited use. Ceramic materials such as calcium fluoride and alumina are resistant to attack by gaseous fluorine even at high temperatures, but these lack mechanical strength. Both materials exhibited corrosion rates lower than metals tested at the same temperature and can be used where physical properties of ceramic materials can be tolerated. Recent work using TiC cermet and fused coatings of CaF_2 + LiF + NiF_2 on alumina has been encouraging.

Organic Polymers (1-2) - Organic polymeric materials are generally not suitable for service in liquid fluorine. Some fluorinated polymers have found limited service at moderate pressures with gaseous fluorine. Impurities introduced in the manufacturing process appear to be responsible for accelerated decomposition of Teflon in liquid fluorine service.

*Parenthetical enclosures refer to Propellant Rating Chart, Page 1-11.

Lubricity (1-2)* - Recent work at NASA Lewis on pumping of liquid fluorine has shown excellent results using liquid fluorine as the lubricant and alumina and titanium carbide as the rotating shaft seals. These materials showed no reaction with liquid fluorine and adequately performed their functions as seal materials.

Effects of Leakage (1) - Leakage of fluorine represents potential toxic, fire, and explosion hazards. The threshold limit value of fluorine is 0.1 ppm; it reacts vigorously with most substances at ambient temperatures, frequently with immediate ignition. Space leakage of propellants is discussed under the section for hydrazine.

Soft Seats (1-2) - Under static conditions, fluorocarbon plastics are satisfactory for liquid fluorine service. Limited applications of some fluorinated soft seat materials (Teflon) have been found for dynamic flow conditions; however, it is recommended that the material be shielded and a minimum of surface area exposed to liquid fluorine.

Hard Seats (2) - Valves having metal-to-metal seats have been used quite extensively in handling fluorine. It is desirable to use dissimilar materials to obtain a good seal and to prevent galling or binding when the valve is operated. Because metal valve seats are not as leak tight as those which utilize a resilient material, the use of double valving is recommended for cirtical applications.

Disconnect (2) - Further availability tests and evaluations are required before a more realistic prediction of performance can be made. Icing due to water vapor in the atmosphere can cause problems in disengagement of the separable units.

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*Parenthetical enclosures refer to Propellant Rating Chart, Page 1-11.

TABLE 1-21. LIQUID FLUORINE (LF_2)

COMPATIBILITY OF MATERIALS

ALUMINUM ALLOYS	TEMP °F	CLASS
1100	-320	1
2017	-320	11
5052	-320	11
6061	-320	1
7079	-320	1
STAINLESS STEELS		
304	-320	1
316	-320	1
347	-320	1
410	-320	1
420	-320	1
PH 15-7 Mo	-320	1
AM 350-C,CX,D,DX	-320	1
Carpenter 20	-320	1

OTHER METALS	TEMP °F	CLASS
A-Nickel	-320	1
Brass (Yellow)	-320	1
Brass (Cartridge)	-320	1
Brass (Casting)	-320	11
Copper	-320	1
Copper-10% Nickel	-320	1
Copper-30% Nickel	-320	1
Everdur 1010	-320	1
Magnesium Alloy AZ-31	-320	1
Magnesium Alloy HK-31	-320	1
Magnesium Alloy HM-31	-320	1
Monel	-320	1

NOTE: Materials listed above are rated compatible based on corrosion resistance and shock sensitivity; they do not include effects of cryogenic temperatures on the materials mechanical properties.

Class 1 Metals listed above are rated compatible based on a corrosion rate of less than 1 mil per year and the material does not cause decomposition, and is free from impact sensitivity. Non-metals are rated for satisfactory service for general use.

Class 11 Materials which exhibit corrosion rates as great as 5 mils per year.

LIQUID OXYGEN (LOX)

Liquid oxygen is a non-toxic, nonflammable, and non-explosive oxidizing agent having a reactivity much lower than gaseous oxygen. Mixing of liquid oxygen with a hydrocarbon fuel will cause the latter to solidfy. The resulting mixture is extremely shock sensitive.

Most metals are not corroded by liquid oxygen; however, the low temperature of liquid oxygen (-300°F) does cause embrittlement of some metals, expecially the body-centered ferrous alloys. As a result, the alloys most commonly used in liquid oxygen handling equipment are nickel, Monel, copper, aluminum, the 300-series of stainless steels, brass, and silver solder.

Of all the metals studied to date, titanium exhibits the greatest sensitivity to impact when immersed in LOX. Battelle Memorial Institute studied the reactivity of metals with liquid and gaseous oxygen and found that only zirconium shows similar reactions to that of titanium. Aluminum and the stainless steels were found to exhibit almost no reactivity in oxygen, although aluminum will ignite under conditions of high explosive shock. Magnesium shows reactivity to explosive shock lying about midway between that of aluminum and tatanium. Following is a partial summary of the results reported by Battelle for titanium.

The sensitivity of titanium approaches that of many organic materials, particularly when the surfaces are not completely cleaned or particles of dirt or grit are present. Reactivity is observed in liquid oxygen and mixtures of liquid oxygen and liquid nitrogen and mixtures of liquid oxygen and liquid nitrogen at impact forces of 20 ft-pounds until the LOX concentration is reduced to 30 percent. Titanium can be partially protected from reactivity in LOX under impact by certain protective coatings, provided these coatings are not broken. Electroless copper and nickel coatings are best, although protection also is provided by nitroding which adds a protective film, and by annealing which increases the oxide film thickness.

When a titanium vessel containing LOX or gaseous oxygen is ruptured by a bullet, a simulated micrometeoroid, or other mechanical puncture, violent burning begins at almost zero pressure (gauge). If the vessel is not fractured by application of external impact, vibration, acoustic or thermal energy, no reactivity is noted. Slowly propagated cracks, such as fatigue cracks, also do not cause reactivity.

The mechanism for the Ti-O_2 reaction is described as a reaction between a freshly formed titanium surface and gaseous oxygen. Titanium exhibits no great reactivity in LOX when deformed by compression, by exposure of a fresh surface by machining or rupture, or by exposure of bulk titanium to high-pressure or high-velocity LOX. In gaseous oxygen, however, titanium is highly reactive when a freshly formed surface is exposed at even moderate pressures. Under conditions of tensile rupture, a pressure of approximately 100 psig will initiate a violent burning reaction with titanium from about -250°F up to room temperature. When 2 percent HF is added as an inhibitor or 5 percent argon as a diluent, the pressure must be increased approximately twofold at room temperature before reaction occurs. Titanium could not be made to react even at very high pressure when the oxygen content was 35 percent or less.

All valves require insulation to avoid evaporation losses. Drainage of condensed water on valves should be provided to avoid water entrapment which may cause corrosion, or valve malfunction if the water refreezes.

Discussion of Problem Areas -

Liquid Oxygen (O_2)

Organic Polymers (2)* - Organic materials should be avoided whenever possible with both liquid and gaseous oxygen because of possibilities of explosion. Currently there are no tests which give a reliable compatibility rating for organic materials in liquid oxygen. Although there are several

*Parenthetical enclosures refer to Propellant Rating Chart, Page 1-11.

lists of organic materials rated as suitable for use with liquid oxygen, specific conditions such as compatibility, impact sensitivity, and embrittlement at cryogenic temperatures should be thoroughly and carefully studied before any organic material is utilized. Sources of energy also may be from operation of mechanical parts, such as; 1) heat produced by friction of metal surfaces, 2) heat from shearing of liquids, 3) shock waves, and 4) heat generated by the catalytic breakdown of an organic material in contact with the metal surface, etc.

The most reliable organic materials for liquid oxygen applications are the fluorinated organic compounds (the more highly fluorinated the compound, the more stable** to attack by liquid oxygen). In special applications many other organic compounds are used, even though these materials have shown to be sensitive to LOX. However, investigations with satisfactory testing procedures are needed before organic materials can be used with liquid oxygen with any great assurance of success.

Currently, there is no single test or group of tests which gives a reliable, uniform compatibility rating for materials suitable for use with liquid oxygen because of difficulty in determining impact sensitivity. Much of the data which are avilable were based on the ABMA 70 ft-lb acceptance level for impact sensitivity. This requirement was designed for application to materials used in missiles, based on the impact threshold level of a particular lubricant which, at the time, was considered to be theonly safe available lubricant. Because of the lack of a technical basis for the establishment of the 70 ft-lb as an acceptance test parameter, and because the size, shape and cleanliness of the sample and test apparatus, as well as the design of the testing machine affect the detonation results, little can be assigned to published compatibility tables. Battelle has indicated that Teflon and Kel-F are the preferred plastics; with a combination of the two most desirable from the standpoint of ductility and strength. Picatinny reports that a polyurethane adhesive

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**The word stable here is more applicable than resistant because it deals with impact sensitivity and not resistance to corrosion.

has been found to be LOX compatible under ABMA procedure. A TFE-FEP hot melt adhesive was also reported to be the only insensitive adhesive when used in direct contact with LOX, but requires a 700°F bonding temperature. Becuase of the apparent need of individual use-tests for each design, no compatibility tables are included in this report.

Wet and Dry Lubes (1)* - No completely compatible lubricants have been found. Selected perfluorinated hydrocarbon and dry lubricants have found limited use; however, the possibility of detonation still exists.

Lubricity (2) - Satisfactory low-load, short-life bearing and gear operation was possible where liquid oxygen was used as a lubricant. While some of the metals of construction proved satisfactory for use with liquid oxygen, others, under stress, tend to become brittle.

Effects of Leakage (2) - Liquid or gaseous oxygen does not display hazards similar to those encountered with most other oxidizers. Pure oxygen is incapable of burning or detonating, but mixed with a material that will burn, the resulting fire is intensified. Gaseous mixtures of oxygen and fuels form a potentially dangerous mixture which can be ignited by any form of spark. Liquid oxygen, when in contact or mixed with any form of combustible material, such as fuels, wood, plastics, oil, lubricants, or paper, forms an explosive mixture and even when frozen may be detonated by static electricity, mechanical shock, or similar energy source. Oxygen is non-toxic; however, contact with liquid or gaseous oxygen close to its boiling temperature will cause severe frostbite. Space conditions and leakage are discussed under this section for hydrazine.

Soft Seats (2) - Because of the composition of soft seat materials, they should be avoided in liquid oxygen service. Although some fluorinated plastics have been found reliable, until satisfactory testing procedures are available, there remains doubt about compatibility tests.

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*Parenthetical enclosures refer to Propellant Rating Chart, Page 1-11.

Disconnects (2) - Pneumatically operated disconnected valves used on missiles presented problems due to icing caused by condensed water vapor in the atmosphere, requiring extensive effort to disengage. In space transfer of the propellant, "freeze-up" should not be a problem due to the absence of water vapor in space atmospheres. Disconnects of the pull-away type during liftoff caused few problems, except for minor leakage.

LIQUID HYDROGEN (H_2)

Liquid hydrogen is a colorless, odorless liquid that normally does not present an explosive hazard when it evaporates and mixes with air in an unconfined space. However, an unconfined mixture of hydrogen gas and air will burn if exposed to an ignition source such as a spark. Liquid hydrogen is not in itself explosive, but reacts violently with strong oxidizers. If it is contaminated with oxygen, it becomes unstable and an explosion is likely to occur. Reaction with fluorine and chlorine trifluoride is spontaneous. Two species of liquid hydrogen exist: ortho-hydrogen and para-hydrogen.

At the low temperature (-423°F) at which hydrogen is a liquid, corrosive attack on materials is not considered to be an important factor in selecting materials to be used. A more important factor in selecting the materials for use with liquid hydrogen is the embrittlement of some materials by the low temperature of the liquid. Embrittlement of some materials by the low temperature of the liquid requires selection of materials on the basis of their structural properties, i.e., yield strength, tensile strength, ductility, impact strength, and notch sensitivity. The materials must also be metallurgically stable so that phase changes in the crystalline structure will not occur either with time-or temperature-cycling. It is known that body-centered metals (such as low-alloy steels) undergo a transition from a ductile to brittle behavior at low temperatures; therefore, such metals are generally not suitable for structural applications at cryogenic temperatures. Face-centered metals, such as the austenitic stainless steels, normally do not show a transition from a ductile to a brittle behavior at low temperatures. For this reason, these types of materials are desirable for use in cryogenic applications; however, care should be exercised in selection of face-centered metals. Low temperature toughness is not a characteristic of all face-centered metals, nor is it a characteristic of all conditions of a specific metal. For example, severely coldworked or sensitized (carbide precipitation at grain boundaries) austenitic stainless steels can become embrittled at low temperatures.

Table 1-22 lists those materials which are considered to be compatible with liquid hydrogen for long-term application.

Discussion of Problem Areas -
Liquid Hydrogen (H_2)

Organic Polymers (1-2)* - The ability of polymeric materials to maintain satisfactory physical properties and to withstand thermal stress caused by large temperature changes is of prime importance. The use of a selected few organic plastics is thus limited to service where embrittling effect at the low temperatures of liquid hydrogen is minimized. Specifically, lip seals constructed of Teflon and Kel-F, static seals an some rubbers, and diaphragm seals from Mylar have proved serviceable. Studies at the National Bureau of Standards have shown that some elastomeric seals under compression retain their sealing capabilities effectively well below the normal brittle point of the polymer without compression.

Wet and Dry Lubes (1) - Lubricants are generally not practical in the presence of liquid hydrogen since they solidify and become brittle at the temperatures involved.

Lubricity (2) - Liquid hydrogen can be utilized as a lubricant under low-load, short-life conditions. Severe surface failure will occur, however, if the service conditions are such that local heating of the contact surface is allowed. The stainless steels are particularly susceptible to surface failure, as are other materials with low thermal conductivities. (Wear rates are reduced drastically by coating one of the surfaces with Teflon or Kel-F). Coldwelding has also been found to occur in gate valves having seats and wedges of 304 stainless in cryogenic service.

Effects of Leakage (2) - The leakage of hydrogen gas does not appear to present problems of an unusual nature, even though the composition limits for combustion are very wide. Hydrogen, being very light, tends to

*Parenthetical enclosures refer to Propellant Rating Chart, Page 1-11.

dissipate rapidly. Proper ventilation and elimination of sources of ignition reduce danger of detonation. An explosion hazard exists when the hydrogen-air mixture is completely or partially confined. Effects of leakage in space are discussed under this section for Hydrazine.

Disconnects (2)* - See comments under Liquid Oxygen.

TABLE 1-22. LIQUID HYDROGEN (H_2)

COMPATIBILITY OF MATERIALS
FOR LONG-TERM APPLICATION

ALUMINUM ALLOYS	OTHER METALS
1100	Molybdenum
1100T	Nickel
2024T	Monel
4043	Inconel
5052	Low Carbon Steel
	High Nickel Steel
STAINLESS STEEL	Titanium
301	
302	NON-METALS
303	Nitryl Rubber
304	Silicone Rubber
304L	Teflon
316	Garlock Packing
321	Bakelite
347	Micarta
410	Lucite
Haynes 21	Graphite

NOTE: The above listed materials were rated compatible primarily for their embrittlement properties at cryogenic temperatures. Non-metals shown as being compatible should be restricted for "warm" joint application or equivalent.

*Parenthetical enclosures refer to Propellant Rating Chart, Page 1-11.

LIQUID OXYGEN-LIQUID FLUORINE MIXTURES (FLOX)

Mixtures of liquid fluorine and liquid oxygen (FLOX) have received some consideration as oxidizers. A typical mixture contains 80 percent fluorine and 20 percent oxygen. There is limited compatibility data for these mixtures, but results of work done at various installations suggest that any material that performs well in liquid fluorine service will also work in FLOX. Evaluation of Atlas components showed no serious problems, except for the replacement of valves with constricted passageways.

The problem areas for FLOX are considered to be the same as those for fluorine, and the reader is referred to that section. Table 1-23 lists the limited compatibility data accumulated to date for FLOX.

TABLE 1-23. LIQUID FLUORINE-LIQUID OXYGEN (FLOX) COMPATIBILITY OF MATERIALS AT -320°F[a]

FLOX-40 (40% F_2 - 60% O_2)	FLOX-20 (20% F_2 - 80% O_2
MATERIAL	MATERIAL
Aluminum 2014-T6	Aluminum 2014
Aluminum 5052-H34	
Aluminum 6061-T6	Cadmium Plated 4037 Steel
4340 Steel	
301 Stainless	
304 Stainless	
347 Stainless	
Monel	
Inconel X	

(a) These materials exhibited less than 1 mil per year corrosion rate, do not cause decomposition, and are impact insensitive.

GELLED PROPELLANTS

LIQUID GELLED PROPELLANTS

A gelled propellant is any liquid propellant which has been conditioned so that it exhibits non-Newtonian properties. So many propellants have been gelled (e.g., hydrazine, RP-1, nitrogen tetroxide, etc.) that it is impossible to make any generalized statements about the compatibility of the gels, as such, with other materials. However, as a rule the additives needed to cause gelling (carbon black, silica, etc.) are not reactive and do not modify the chemical characteristics of the parent propellant, so that the compatibilities of gel can be considered to be the same as those of the parent propellant with respect to the action of the propellant on the system. Recently, studies on some gelled systems has indicated that the degradation of the propellant by system materials or impurities has been decreased by the gellation. Current work has been concentrated on finding more efficient gellation agents, in order to increase combustion efficiency and storage life.

One type of gelled propellant is characterized by thixotropic properties; that is, the viscosity of the propellant decreases with increasing shear and stress decreases with time at constant shear. These properties are of interest for several reasons. For example, when the propellant is locked in a tank, there is no shear being applied and the propellant is very viscous. When pressure is applied and the propellant valve is opened, shear stresses are induced, viscosity is reduced, and the propellant flows. As the propellant flows through the tank, valves, feed lines, and injector orifices, the shear becomes greater, the viscosity becomes less and the propellant behaves more like a low-viscosity liquid. From the standpoint of safety, the highly viscous state of the propellant when locked in a nonpressurized tank is advantageous.

The properties of gelled propellants also present some problems. For example, a relatively thick coating of propellant may adhere to tank and valve walls. Pressure drops through lines, valves and other components

are larger than those of comparable liquids. Valve maintenance and cleaning may be difficult if there are inaccessible cavities where gel may collect. Gels also may break down under the influence of radiation, temperature extremes, or inclusion of impurity electrolytes.

Excessive cold working (i.e., pumping into run tanks, over-mixing, etc.) can reduce the strength of the gel to an unacceptable value. Evaporation of the propellant can leave a fine powdery residue which could interfere with the normal action of moving parts such as valve stems.

Gelled propellant systems will probably be schematically similar to liquid propulsion systems which perform the same task. In general, it can be stated that the interaction between typical valve configurations and gelled propellants is not overly severe and that the associated problem areas can be circumvented through the use of proper design techniques.

Discussion of Problem Areas -

Liquid Gelled Propellants

Metals and Ceramics (3)* - No real problem is envisioned with selecting metals suitable for use with liquid gels. It has been demonstrated that metals compatible with the liquid constituent will serve equally as well for gelled propellants.

Organic Polymers (2) - As with metals, it is necessary to select polymeric material based on the compatibility of the liquid constituent since the gelling agents are present in very small quantity and are normally inert materials.

Wet and Dry Lubes (2) - Compatibility of lubricants with gelled liquids depends on the compatibility of the liquid constituent.

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*Parenthetical enclosures refer to Propellant Rating Chart, Page 1-11.

Lubricity (2) - Experimental flow systems on both real and simulated systems has shown that it is reasonable to consider that the gelled liquid will have lubricating properties similar to those of the liquid constituent. These properties are the result of solvent characteristics and reducing properties of the liquid constituent under a frictional force.

Viscosity (2)* - Viscosity varies with shear force (i.e., velocity, tube diameter). This presents a definite problem of retention in pockets and cavities of components, resulting in poor propellant utilization and difficulties in cleaning. As discussed previously, proper mechanical design should eliminate most of these difficulties.

Radiation Tolerance (2) - While no major problems have been envisioned for the liquid constituents under consideration for gels, some gelling agents appear to break down under various types of radiation and, in turn, cause the gel to be degraded.

Effects of Leakage (2) - The vapor pressure of the parent propellant is unaffected by gelling, hence toxic hazards of the liquid constituent must be considered. The rate of vapor evolution, however, is reduced, which in turn will reduce fire and explosion possibilities. Leakage, predominantly from volatilization of the high vapor pressure liquid constituent of the gel, will leave a residual powder, the gelling agent, creating problems such as sticking or malfunction of valves.

Control of Flow (2) - Difficulties in accurately measuring flow rate are anticipated; however, it may be expected that pressure drop will generally be higher than for the parent propellant and design allowances may be necessary.

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*Parenthetical enclosures refer to Propellant Rating Chart, Page 1-11.

Shut-Off (1) - A very serious problem exists with the last valve in a system exposed to space environment. Rapid volatilization of the liquid component of a gelled liquid would leave a solid residue possibly of sufficient quantity to produce leakage or sticking of the valve on subsequent operations.

METALIZED GELLED PROPELLANTS

In order to increase the thermochemical performance of rocket propellants, or to increase propellant bulk density for volume-limited propulsion system applications, powdered metals have been added to liquid propellants. The solid phase of these mixtures can be anywhere from 10 to 90 percent by weight. The metallic gel is generally prepared with metal having an average particle size range of 5 to 50 micron so that: 1) its effect on the flow characteristics of the propellant will be minimized, 2) burning in the combustion chamber will be less difficult, 3) suspension in the liquid will be easier. It has been necessary to gel the mixtures in order to suspend the metal powder in the propellant. Like gelled propellants, these metalized gelled propellants often exhibit thixotropic properties. Another similar class of gels employ metal containing compounds as gellants. These systems are more energetic than the straight metallized ones, but exhibit some storage instability.

Because of the solid particles, metalized gelled propellants present problems which are not encountered with standard propellants. For example, abrasive action of the particles could cause galling of the valve stems or scarring of valve seats and plugs. Particles may become trapped between a valve seat and plug, allowing the valve to leak. Evaporation of the liquid phase of the propellant will leave a solid matrix as a residue which can hinder valve operation and restrict propellant flow. The presence of solid particles in the propellant can result in the galvanic corrosion of certain standard materials of construction, particularly in the presence of impurities which allow electrolytic activity to occur. Any intimate contact of the propellant with lubricants could result in the transfer of particles to the lubricant, thereby reducing the effectiveness of the lubricant. In addition, the problems listed previously for non-metalized gels are applicable. Although it is not certain whether special components will be necessary to utlize metalized gels in propulsion systems, modified designs of standard components will be required to reduce the effects of the undesirable characteristics.

Discussion of Problem Areas -

Metalized Gelled Propellants

Metals and Ceramics (2)* - Metalized gels subject certain metal components (i.e., aluminum, nickel, copper) to erosion and/or galling under dynamic conditions. Suitable metals for construction require compatibility with the liquid carrier and relatively high hardness for erosion resistance against the metal constituents of the gel.

Organic Polymers (2) - Considerably greater erosion and galling of plastic materials are anticipated under dynamic conditions. Generally, polymeric materials compatible with the liquid constituent are expected to serve as well under static conditions.

Wet and Dry Lubes (1-2) - Gels containing metal particles have considerably greater abrasive action under dynamic flow resulting in greater "wash-out" of lubricants. For static conditions, the restrictions placed upon the liquid constituent dictate selection of a compatible lubricant.

Lubricity (1) - The incorporation of metal particles in a gelled propellant tends to decrease the lubricating properties due to the added abrasive nature of such metals.

Viscosity (2-3) - As with gelled liquid propellants, viscosity varies with shear force and presents problems of propellant uitlization, cleaning and greater pressure drop in components. Recent tests were performed by Edwards AFB on metallized propellant simulants in order to define the problem areas in pumping a metallized gelled propellant. Prior to testing, the pump start transient performance was considered to be the greatest potential problem area. Test results indicate, however, that pump start transients with a metallized gel compared favorable with those obtained with a Newtonian fluid. The pump cavitation performance was unaffected by

*Parenthetical enclosure refers to Propellant Rating Chart, Page 1-11.

the presence of solid particles in the test fluid. Considerable erosion of the aluminum pump hardware was encountered during testing with the simulated propellant; however, they considered that there was a good indication that the use of steel hardware would solve the problem.

Radiation Tolerance (2)* - Some gelling agents appear to deteriorate under radiation and in turn cause the gel to be degraded.

Effects of Leakage (1) - Loss of the liquid component of the gel by leakage will leave a solid matrix to interfere with proper operation of a component. The volatile liquid component will still present toxic, fire, and explosion hazards, but to a lesser extent due to the probable slower rate of evolution.

Control of Flow (1) - No satisfactory way has been found to measure flow rate accurately.

Soft Seats (1-2) - It is anticipated that the metal particles of gels will have detrimental effects on soft seats. Metal particles, trapped against the valve seat when the valve is closed, can cause the valve to leak initially or after several cycles. Selection of seat material should be based principally on compatibility with the liquid constituent of the gel.

Hard Seats (2) - Metal particles of the gel may prevent valves utilizing hard seats from complete sealing, and under dynamic flow the metal particles may result in considerable erosion of the seat by abrasive action.

Shut Off (1) - As with liquid gels, metalized gels present a serious problem for valves exposed to vacuum conditions because there would remain a greater quantity of residue on volatilization of the liquid constituent.

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*Parenthetical enclosures refer to Propellant Rating Chart, Page 1-11.

REFERENCES - MATERIALS COMPATIBILITY

A number of the propellants of interest have similar compatibility behavior and degradation mechanisms. Because of this, it is felt that the references should be listed numerically and the number referred to for the propellant of interest. Some of the references were general enough in nature to warrant inclusion under a general heading. These references normally include either a general treatise on materials compatibility, or else deal with a large number of the listed propellants. As such, these references should be examined in conjunction with the references for the specific propellants of interest. A compilation of reference numbers for specific propellants given in Section B, unless otherwise noted, are listed as follows:

Reference numbers are for specific propellants, Section B, unless otherwise noted.

EARTH STORABLE PROPELLANTS

1. Hydrazine: 8, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 128.
2. Monomethylhydrazine: 27, 28, 29, 30.
3. Unsymmetrical Dimethylhydrazine: 8, 31, 32, 33,
4. Aerozine - 50: 8, 20, 34, 35, 36, 37, 38, 39, 40, 128.
5. Pentaborane: 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 54.
6. Nitrogen Tetroxide: 8, 20, 23, 38, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 76, 127.

SPACE STORABLE PROPELLANTS

1. Diborane: 54
2. Hybaline A5: 1, 2, 12, 51.
3. Liquified Petroleum Gases: 126; General References Section A - 5, 10.
4. Chlorine Trifluoride: 8, 24, 44, 45, 46, 47, 48, 49, 50.
5. Chlorine Pentafluoride: 24, 51.
6. Oxygen Difluoride: 52, 53, 106, 108, 109, 110, 111, 112, 113.
7. Perchloryl Fluoride: 24, 48, 49, 55, 56, 57, 58.
8. Nitrogen Trifluoride: 21, 129, 130.
9. Nitryl Trifluoride: 21, 129, 130.
10. Tetrafluorohydrazine: 21, 129, 130.
11. Liquid Fluorine: 50, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105, 106, 107, plus Section C: "Bibliography of Fluorine Reports."
12. Liquid Oxygen: 40, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95.
13. Liquid Hydrogen: 74, 75, 76, 77, 78, 79, 80, 81, 82.
14. Liquid Oxygen-Liquid Fluorine Mistures: 106, 113, 114, 115, 116, 117, 118, 119, 131
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II. CLOGGING OF FILTERS AND ORIFICES

Problems identified with flowing N_2O_4 through small clearances were previously investigated by TRW Systems for NASA under Contract NAS 7-107[1]. Several instances of valves sticking and jamming, filters clogging and flow stoppage were encountered when flowing N_2O_4. These problems were attributed to a contaminant residue described as a fine brownish powder. Studies conducted under the NASA program led to postulation that the residue was the result of gel precipitates from N_2O_4. The gel material, upon drying crystallized to a powdery residue.

Further work was undertaken by TRW Systems for NASA under Contract NAS 7-549[2] with the objective of producing the clogging material under laboratory conditions and determining the behavior of the material. The program results showed N_2O_4 formed a gel-like material at the entrance to capillaries and filters causing flow decay to the extent of complete blockage.

Other investigations have also reported flow decay due to the formation of clogging material in N_2O_4. Rocketdyne under AFRPL sponsorship, Contract AF04(611)11620[3], reported the formation of solid crystalline precipitates from flowing N_2O_4 through a valve orifice. The solid precipitate deposited on a pintle used for throttling the flow. Another case of flow decay was reported to result from the formation of an oily, highly viscous residue found on screens during rocket engine component testing. One other report[4] described the formation of gelatinous material in clogging of small orifices during high velocity flow of N_2O_4. At least two cases of formation of gel-like material have been known to occur in rocket engine components flowing hydrazine fuel.

This section presents a summary of the work performed under the NASA NAS 7-549 contract. Gel formation was observed to form at the entrance to a 0.005 inch diameter glass capillary during flow with N_2O_4. Figure 2-1, taken from Reference 2, is an enlarged photograph at the entrance to the capillary showing the gel formation. The propellant was specification grade MSC-PPD-2A N_2O_4. Table 2-1 presents a summary of the test data for several runs made on 0.005 inch and 0.010 inch diameter capillaries. In several of the test runs the N_2O_4 was temperature conditioned by flowing the propellant through a heat exchanger. Movies were taken during the flow runs which showed the buildup of blockage material and was described as a slow pulsating, turbulent, twisting of material at the capillary entrance.

Gel formation was also observed to form on filters. Figure 2-3 illustrates the filter condition in the as-received condition. Figure 2-2a is a photograph of the clogged filter and Figure 2-2b is a photograph showing the powdery residue after the gel dried. The filter used was a 2μ nominal - 10μ absolute 316 wire mesh cartridge type. A summary of the test run data is presented in Table 2-2 and flow decay curves are presented in Figure 2-4. The N_2O_4 used in the filter test runs were MSC-PPD-2A N_2O_4 and MSC-PPD-2A N_2O_4 doped with zinc and iron nitrate. Analyses of the blockage material showed iron was the only metallic constituent detectable in the dried residue from the undoped MSC-PPD-2A N_2O_4 and iron and zinc were the only significant metals found in the residue of the doped N_2O_4.

A gel-like material was found in the line of a rocket engine at TRW Systems after flowing hydrazine fuel. The material was deposited on a fitting junction at the entrance of the control valve. At this time there is no definition as to the mechanism of this formation or to its relationship with the gel formation with N_2O_4.

REFERENCES

1. "Advanced Valve Technology for Spacecraft Engines," Final Report, TRW Report No. 8651-6042-SU-000, Contract No. NAS 7-107, August 1965.

2. "Investigation of the Formation and Behavior of Clogging Material In Earth and Space Storable Propellants," Interim Report No. 08113-6007-R000, Contract No. NAS 7-549.

3. Rocketdyne, "Method for Elimination of Corrosion Products of Nitrogen Tetroxide," Final Report, Contract AF04(611)-11620, July 1967.

4. P. Pomerantz, "Nitrogen Tetroxide for NASA Small-Engine Applications," Special Report (Technical), NASA Western Operations Office, May 17, 1965.

TABLE 2-1. Test Data Summary on Flow Behavior of MSC-PPD-2A N_2O_4 Using Capillary Test Sections

CAPILLARY I.D. INCHES	ASPECT RATIO (length/dia.)	DIFFERENTIAL PRESSURE ACROSS TEST SECTION, PSI (DOWNSTREAM PRESSURE MAINTAINED AT 10 PSIG)	HOLD TANK TEMPERATURE, °C	INLET TEST SECTION TEMP. °C	DIFFERENTIAL TEMPERATURE FROM HOLD TANK TO INLET TEST SECTION, °C	EXIT TEST SECTION TEMP. °C	REMARKS
.005	200	50	22	24	2	24	FLOW BLOCKAGE
.005	200	20	22	22	0	22	FLOW BLOCKAGE
.005	100	54	24	24	0	24	FLOW BLOCKAGE, MOVIES TAKEN
.005	100	62	23	23	0	23	FLOW BLOCKAGE, MOVIES TAKEN
.005	100	91	23	24	1	24	GEL FORMATION, BUT MATERIAL BLOWN THROUGH CAPILLARY, MOVIES TAKEN
.005	100	102	34	22	12	25	GEL FORMED, BUT MATERIAL BLOWN THROUGH
.010	100	10	23	24	1	24	MATERIAL BUILD-UP, BUT BLOWN THROUGH AT HIGHER PRESSURES
.010	100	25	23	23	0	23	MATERIAL BUILD-UP, BUT BLOWN THROUGH AT HIGHER PRESSURES
.010	100	32	23	23	0	23	NO BUILD-UP OR BLOCKAGE
.010	100	52	24	24	0	23	NO BUILD-UP OR BLOCKAGE, MOVIES TAKEN
.010	100	63	59	14	45	18	NO BUILD-UP OR BLOCKAGE
.010	100	60	50	0	50	7	NO BUILD-UP OR BLOCKAGE
.010	100	196	22	22	0	24	NO BUILD-UP OR BLOCKAGE, MOVIES TAKEN

TABLE 2-2. Test Data Summary of Flow Behavior of N_2O_4 Using 2μ Nominal-10μ Absolute Filters

Run	Hold Tank Temp. °C	Test Section Inlet Temp. °C	Test Section Outlet Temp. °C	Diff. Temp., Hold Tank - Inlet Test Section °C	Test Section Inlet Press., Psia	Test Section Outlet Press., Psia	Diff. Press. Across Test Section, Psia	Original Flow Rate, gal/min	Time For 10% Flow Rate Decay, Sec.*	Time For Complete Blockage (Flow Rate) <0.10 gal/min	Remarks
Neat N_2O_4	26	26	26	0	60	50	10	0.40	30+	---	Flow remained constant at 75% of original for rest of run.
Neat N_2O_4	26	10	10	16	67	54	10	0.31	30+	240	Cloud formed at 300 seconds; gel clearly seen at 390 seconds.
Doped N_2O_4	23	23	23	0	43	27	16	0.77	180	---	Flow had been reduced to 86% of original when N_2O_4 depleted at 300 seconds.
Doped N_2O_4	69	51	51	18	91	62	29	0.76	60+	---	Run terminated at 150 seconds due to cavitation at test section exit.
Doped N_2O_4	32	15	13	17	54	18	36	0.30	150	660	No clearly defined cloud observed; gel clearly seen at 600 seconds.

*Data plotted and smoothed; + indicates flow decayed 10% or more before next data point plotted (normally within 10 seconds).

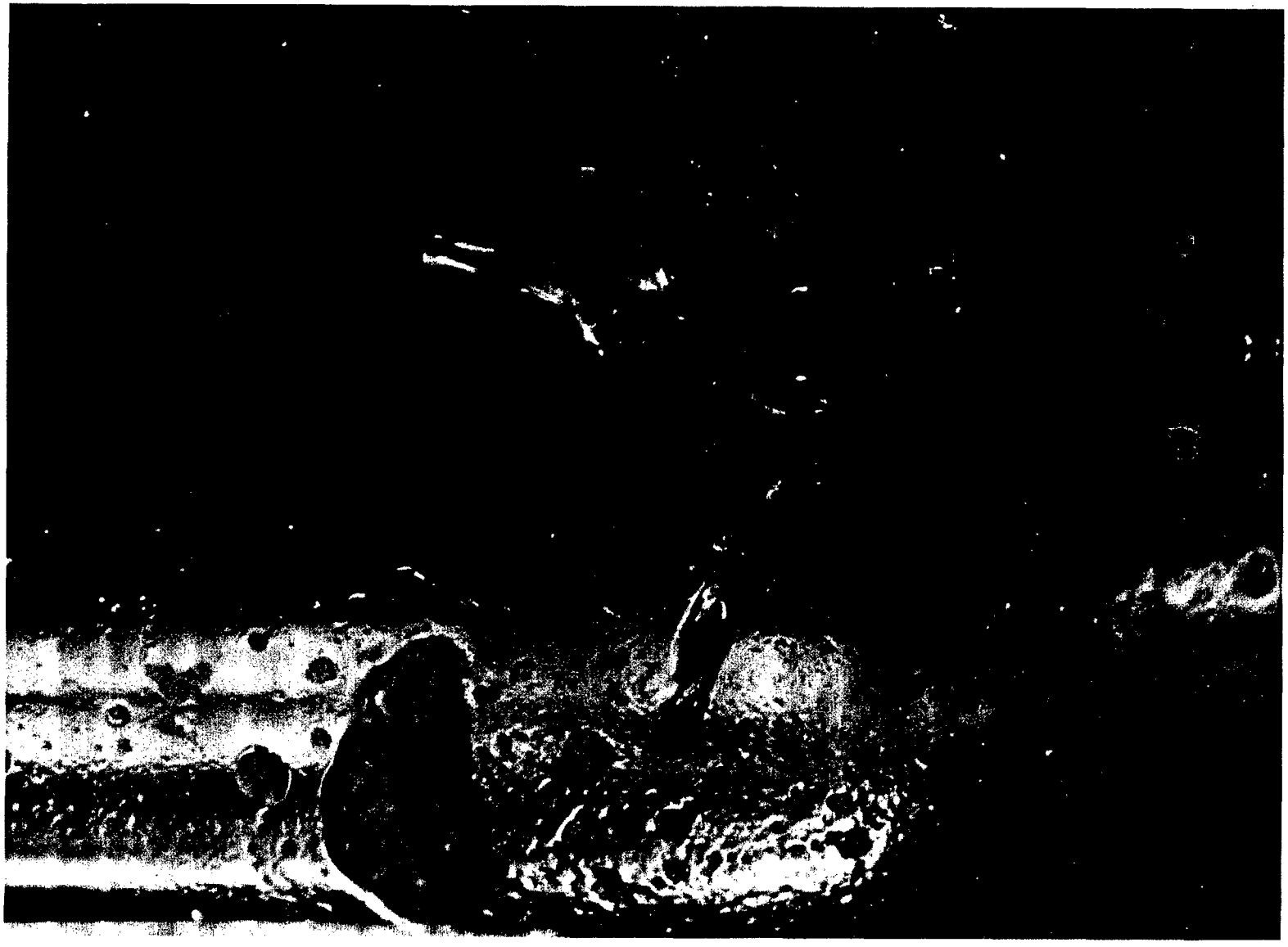
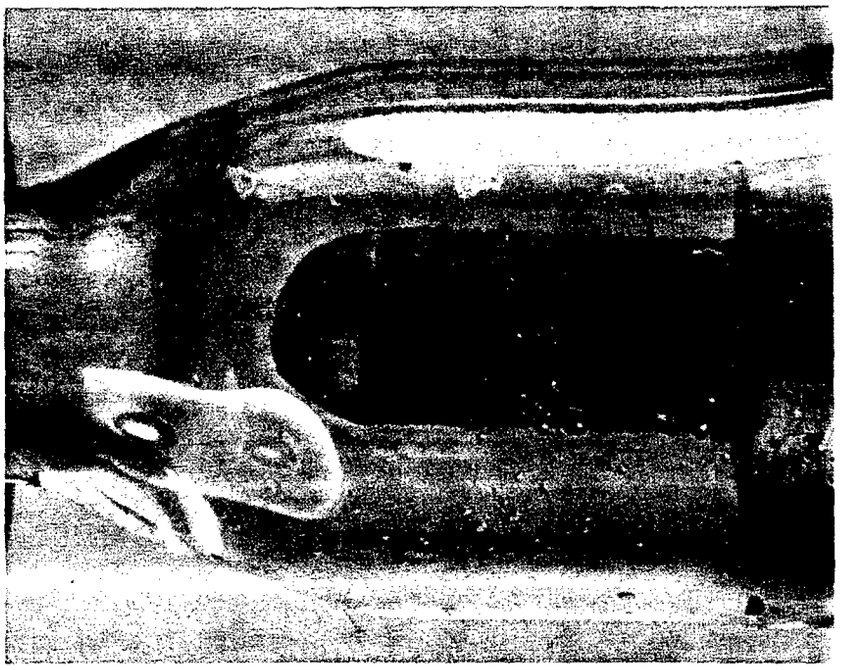
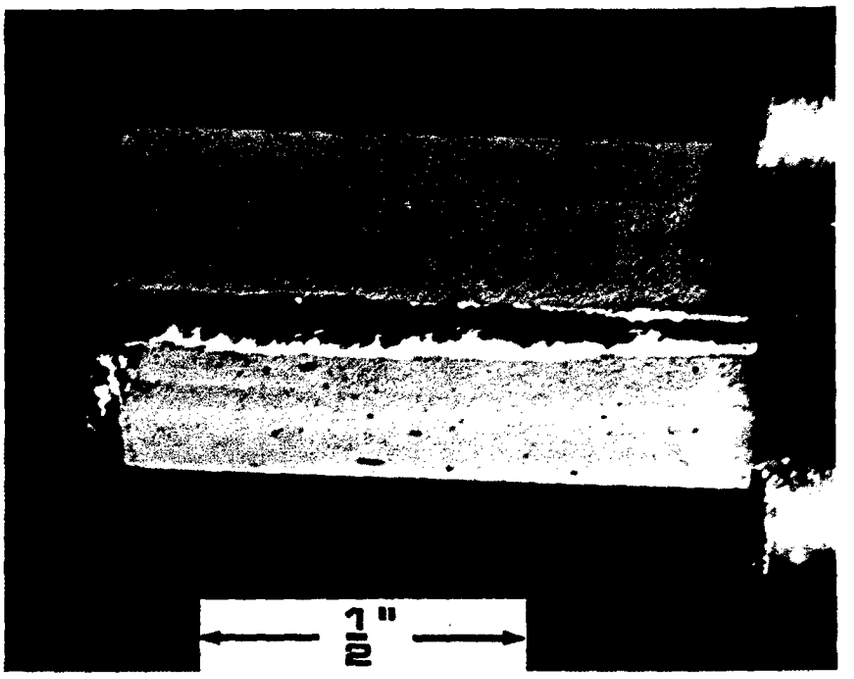


Figure 2-1. Enlarged View of Gel Formation at Entrance to .005" Diameter Capillary Test Section



a. Clogged Filter (2μ - 10μ) Showing Gel Formation During N_2O_4 Flow Runs



b. Clogged Filter After Drying Showing Powdery Residue

Figure 2-2. Photograph of Clogged Filter Before and After Gel Formation Dri

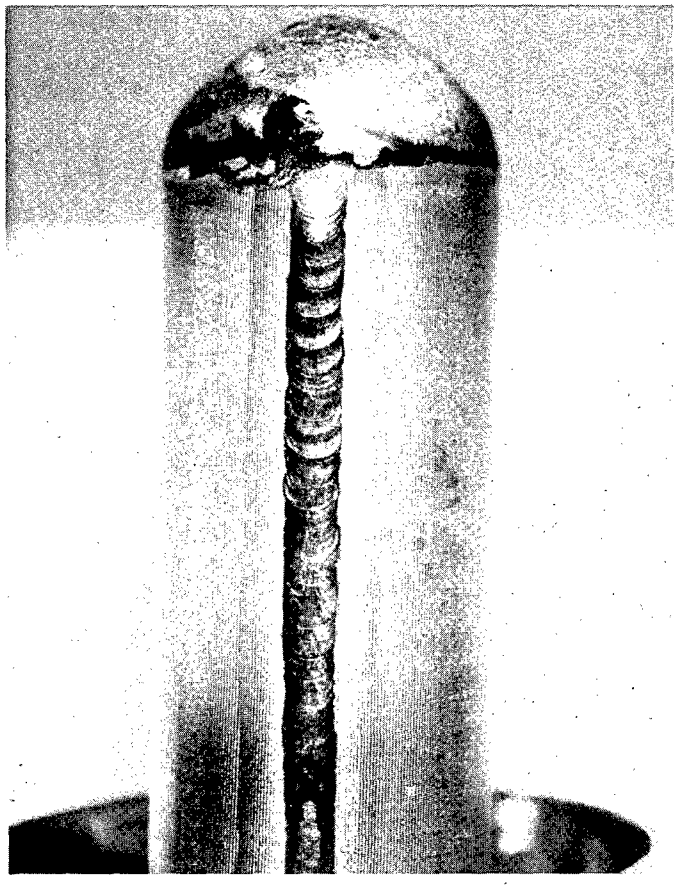


Figure 2-3. Close-up Photograph of Filter

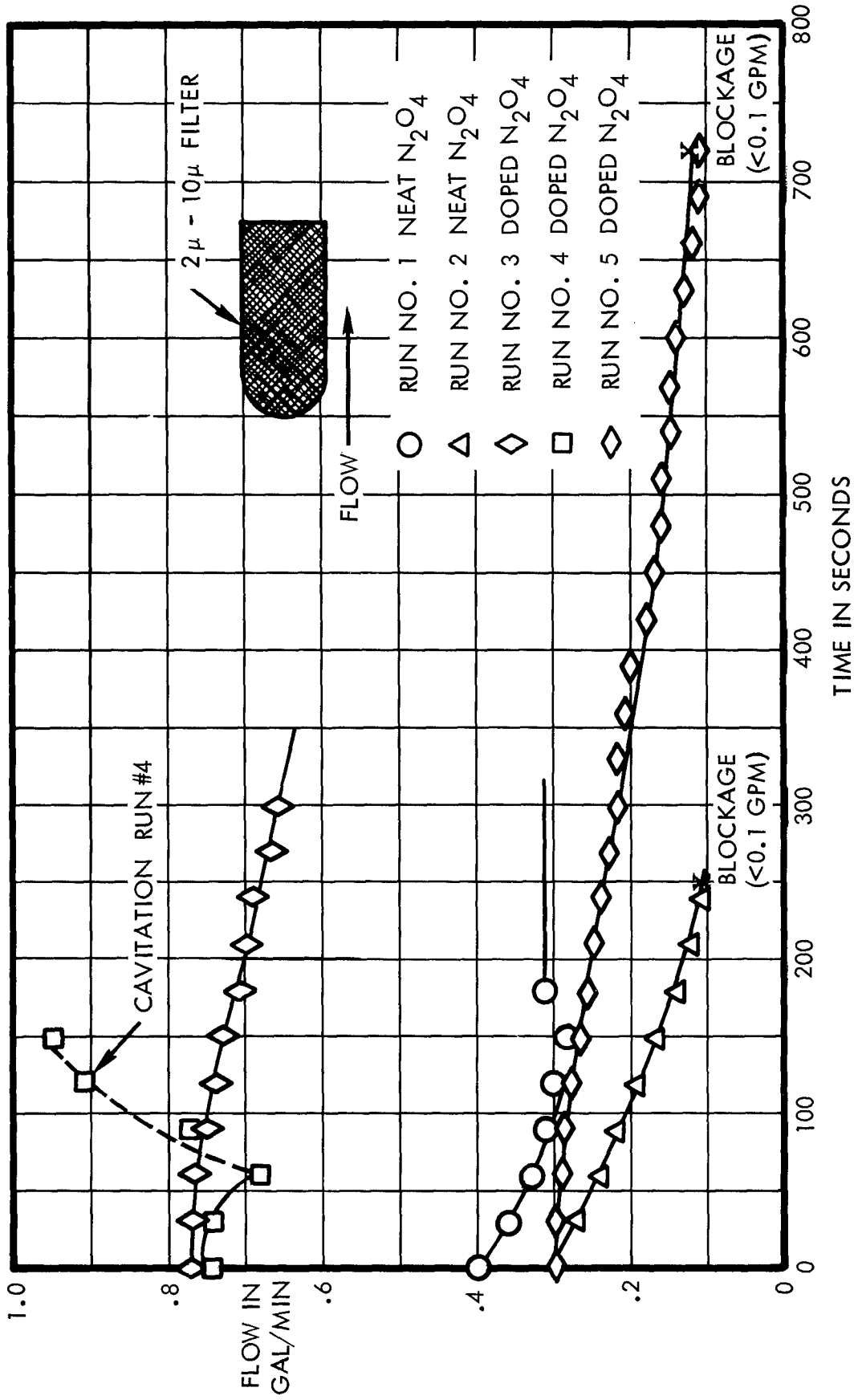


Figure 2-4. Flow Decay Curves for N_2O_4

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